Determination of the Glass Transition of Rubber Samples by Means of DMTA in Compression Mode

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1 EPLEXOR® 500 N

Introduction

Today, the method of Dynamic-Mechanical Thermal Analysis (DMTA) is well established in materials research for rubber and tires. The development about new compounds, e.g., in the tire industry, requires detailed information about the mechanical properties of the materials applied. This includes the determination of visco-elastic material data containing the storage modulus E', loss modulus E" and loss-factor tanδ, as function of the temperature, excitation frequency and external deformation (e.g., strain).

Quite popular is the shore-hardness test. Unfortunately, information about the visco-elastic properties obtained by shore tests is lacking in certain significant areas. Data about temperature and frequency dependency of the compounds is not available at all. Furthermore, the deformation applied to the samples during the shore test is not measured.

Only DMTA investigations are able to yield the desired results. Since the visco-elastic properties (E', E", tanδ) of elastomer systems depend on the externally applied deformation, temperature sweeps must be performed at constant strain amplitudes over the entire application temperature range.

Due to the high stiffness of rubber compounds at temperatures below the glass transition T_g, high force levels are needed in order to obtain the required static and dynamic deformations.

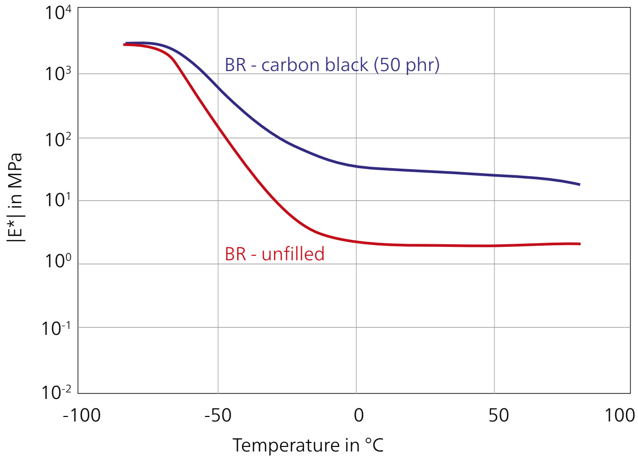
Normally, for compression tests, cylindrical samples ("Roelig" samples) with a height and diameter of 10 mm are used.

Assuming an E' modulus of 3,000 MPa, a typical value in the glassy state, the test capacity of the instrument requires a dynamic force amplitude of +/-50 N to generate a detectable elongation of about 2 µm. This cannot be achieved with classical laboratory DMA instruments. Especially well-suited for these tasks is the EPLEXOR® 500 N by NETZSCH GABO Instruments (see figure 1).

DMTA systems such as the EPLEXOR® series by NETZSCH GABO Instruments are equipped with high-power drives to realize suitable amplitudes of high force levels.

In quality control (QC), however, time-consuming temperature sweeps are inconvenient due to economical reasons. QC tests should be carried out very quickly. A QC test, including sample preparation, should be finished in at most 20 minutes. This application note illustrates how temperature sweeps can be substituted by frequency sweeps, carried out close to the T_g.

NGB · Application Note 092 · E · 03/16 · Technical specifications are subject to change.



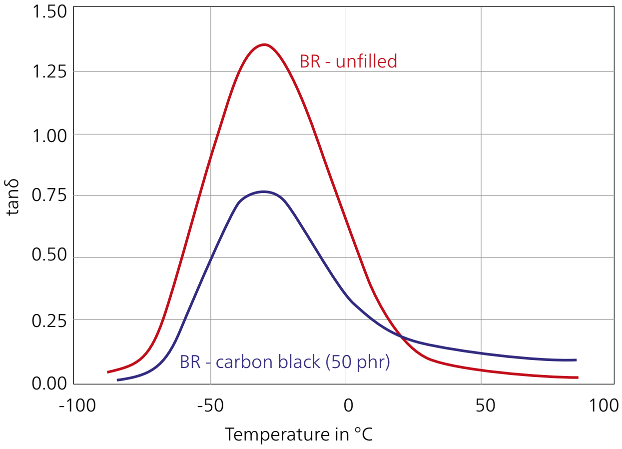
2 Temperature sweep; absolute values of the complex modulus |E*| of a filled and unfilled BR system as a function of temperature (compression mode, static strain: 4%, dynamic amplitude: ±0.2%, frequency: 10 Hz)

Temperature Dependence of Butyl Rubber (BR) and SBR 1500

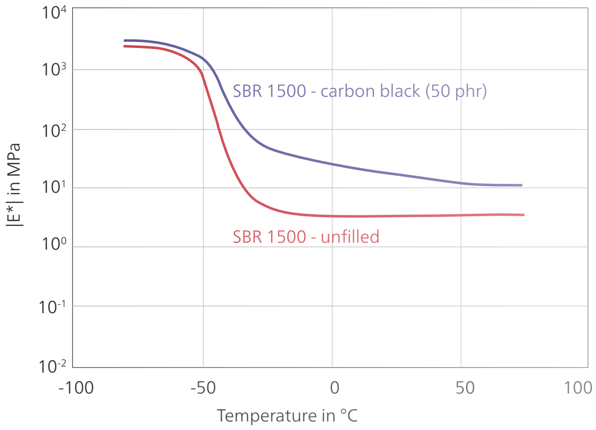
All temperature sweeps are performed at a static deformation of 4% strain as relates to the initial sample length (10 mm for all samples) within a temperature range of -80°C to 80°C. The applied dynamic strain amplitude is ± 0.2%; the test frequency is 10 Hz.

Figure 2 shows the complex modulus of a filled (50 phr carbon black) and an unfilled BR as a function of temperature. Due to the carbon black content, the modulus of the filled BR is about 10 times higher than that of the pure BR at temperatures above 0°C.

The filled and the unfilled BR systems (figure 3) exhibit a very broad glass transition area covering a temperature range of about 50 K (half-width of the tanδ peak). However, the tanδ peak heights of the two systems are significantly different from one another (filled: tanδ peak maximum is 0.75, unfilled: tanδ peak maximum is 1.3).

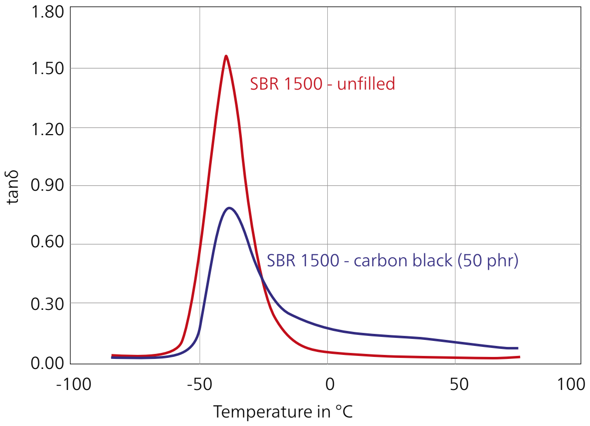


3 Comparison of tanδ of a filled and unfilled BR system as a function of temperature (temperature sweep, same measurement conditions as in figure 2)



4 Absolute values of the Complex modulus [E*] of a filled and an unfilled SBR 1500 system as a function of temperature (comparison) (temperature sweep, same measurement conditions as in figure 2)

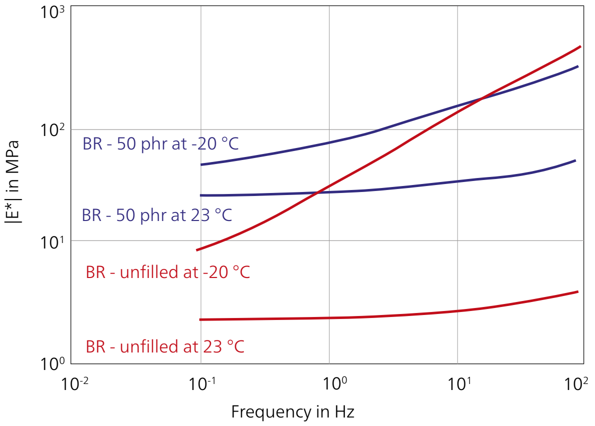
Figures 4 and 5 show the complex modulus and tanδ of the second system investigated. Again, a filled and unfilled system were characterized, but this time based on SBR 1500. The pure SBR exhibits a much narrower glass transition peak than the BR system. The half-width of this glass transition was only 20 K. Like before, the absolute values of the complex modulus [E*] of the unfilled SBR drops down from nearly 3,000 MPa below the T_g to values less than 5 MPa above the T_g. The [E*] of the filled systems is – at temperatures above the T_g – double that of the unfilled SBR 1500.



5 Comparison of tanδ of a filled and unfilled SBR 1500 system as a function of temperature (temperature sweep, same measurement conditions as in figure 2)

Temperature sweeps allow for characterizing different materials. Unfortunately, they are quite time-consuming. Fast and intelligent test procedures, however, which can show differences in the visco-elastic behavior of materials like a “fingerprint” will help reduce the testing times.

Frequency sweeps performed in the glass transition region have proved to be useful techniques.



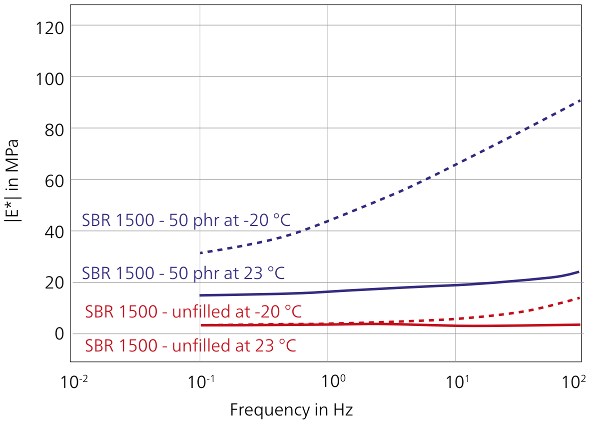
6 Frequency-dependence of a filled and unfilled butyl rubber system (frequency sweep, same measurement conditions as in figure 2)

Frequency Sweeps Performed on Filled and Unfilled Rubber Systems

Figure 6 portrays the frequency dependence of the two butyl rubber systems. The complex modulus (E*, displayed as absolute values) of the filled system (BR - 50 phr at 23°C) is simply shifted to a higher level than that of the unfilled BR (BR - unfilled at 23°C). At ambient temperature, the line shapes of the filled (BR - 50 phr at 23°C) and unfilled (BR - unfilled at 23°C) BR compounds are very similar, indicating the same frequency behavior for the filled and unfilled rubbers.

Within the glass transition region at a temperature of T = -20°C, the situation is quite different. The unfilled BR exhibits a much higher slope of the [E*] curve with increasing frequency than the filled system.

Similar results can be obtained for the filled and unfilled SBR 1500 systems (figure 7). As expected, the filled system (SBR 1500 - 50 phr at 23°C) generally shows higher values for the complex modulus [E*] than the unfilled one (SBR 1500 - unfilled at 23°C). The slope of the two curves at room temperature does not differ much. Again, at -20°C, large differences in the line shape can be detected, which allow one to distinguish between different filler contents by analyzing the absolute values of E* as discussed previously.



7 Frequency dependence of the filled and unfilled rubber SBR 1500 systems (frequency sweep, same measurement conditions as in figure 2)

Summary

Large rubber samples (of 10 mm diameter) can only be investigated in compression mode by using high-force DMA instruments such as the EPLEXOR® 500 N by NETZSCH GABO Instruments.

The question of in what way E* is a function of the carbon black content can be answered with frequency sweeps performed in thermal equilibrium at different temperatures. Due to the principle of time-temperature or frequency-temperature superposition, variation of the frequency while maintaining a constant temperature can supply the same information as a temperature sweep.

Typically, a frequency sweep only requires about 5 minutes, thus accelerating the test procedure drastically over conventional temperature sweeps, which run about 2 hours.

The test results also show that frequency sweeps carried out close to the T_g allow rubber materials of differing carbon black content to be distinguished by rather quick analysis.