EPLEXOR®
APPLICATION 14

A new tool for quality control?
Visco-elastic properties of filled and unfilled rubber systems

Introduction

Nowadays the method of **D**ynamic **M**echanical **T**hermal **A**nalysis **(DMTA)** is quite well established in laboratories of material researchers and in departments of quality control (QC). The development of new compounds within the tyre industry requires detailed information about the mechanical material properties. The determination of visco-elastic material data containing the storage modulus E`, the loss modulus E`` and the visco-elastic loss-tangens tan δ which depend on the temperature, the excitation frequency and the external deformation (e.g. strain), is absolutely necessary.

Quite well established is the shore-stiffness test. Unfortunately, the information about visco-elastic properties obtained by shore tests is very restricted. Data about temperature and frequency dependency of the compounds is not available. The applied deformation during the shore test onto the samples is not measured.

Therefore, only DMTA investigations are yielding the desired results.
Visco-elastic properties (E', E'', tan delta) of elastomer systems depend on the externally applied deformation. Consequently, temperature sweeps have to be performed at constant strain amplitudes within the complete temperature range.

Due to the high stiffness of rubber compounds at temperatures below the glass transition Tg, high forces have to be applied to obtain the required static and dynamic deformation.

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

Assuming a modulus E' of E'= 3000 MPa, as can be observed in the glassy state, the test capacity of the instrument requires a dynamic force amplitude of +/-50 N to measure a detectable elongation of about 2 microns only.

Only DMA systems like Gabo Qualimeter's **EPLEXOR®** series are equipped with high power drives (from **EPLEXOR® 150 N High End** with up to 150 N up to **EPLEXOR® 4000** with 4000 N force capacity).

Material quality control (QC) is another important field of application. In QC time consuming temperature sweeps are inconvenient due to the high cost.

As a standard, QC tests should be carried out very quickly. At least within 20 minutes, including sample preparation, a QC test should be finished.

This applictation note shows the idea to substitute temperature sweeps by frequency sweeps carried out close to Tg.

The first part contains a brief introduction into the method of **DMTA** followed by a description of the **EXPLEXOR®**-series made by Gabo Qualimeter Testanlagen GmbH.

In the second part the temperature sweeps made on BR and SBR 1500 (unfilled, filled with 50 phr carbon black) are shown. In addition frequency sweeps carried out close to Tg are discussed in comparision to frequency sweeps obtained at room temperature.

The DMTA-EPLEXOR® System

The method of dynamic mechanical spectroscopy (DMA/DMTS or DMTS) uses forced mechanical vibrations for the deformation of the specimens. The samples can be tested in tension-, compression-, bending- and shear mode. In case of pure elastic materials the sample response to a dynamic mechanical excitation will be in phase with the driving signal, whereas the response of a pure viscous material will be out of phase (phase shift δ- refer to figure 1). The most polymers show a mixture of elastic and viscous material properties.

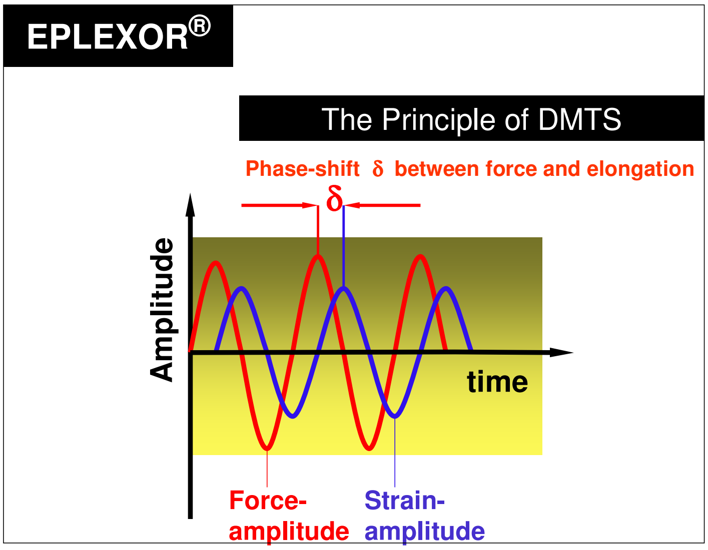

Figure 1 : sample excitation and response to an external periodical signal

Figure 2 shows E' and E'' presented in the complex plane. E', the storage modulus corresponds to the real part of E* which represents the elastic behaviour of the investigated sample, whereas E'', the loss modulus, describes the viscous properties of the sample. E'' corresponds to the imaginary part of E*. The loss-tangens tan δ is related to the phase shift δ between excitation and response.
A metal spring will show only elastic properties, whereas a oil exhibits only viscous behaviour. Most polymers including rubber show an intermediate behaviour as indicated in figure 2.

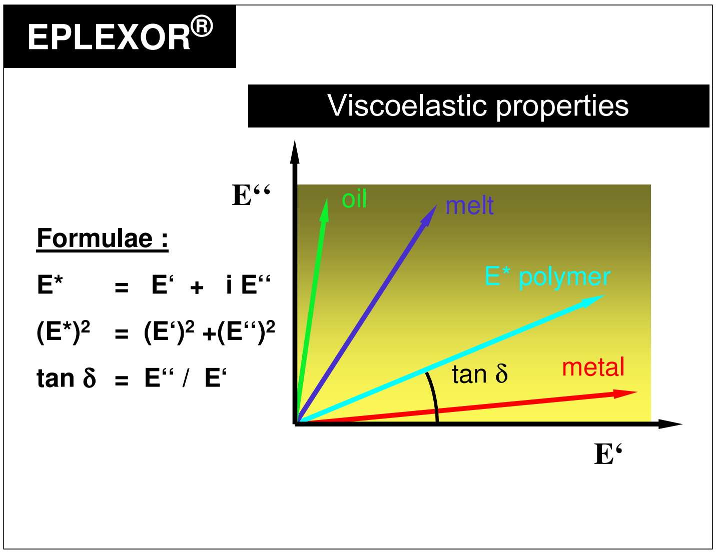

Figure 2 : Complex modulus E* (schematically)

Figure 3 shows the EPLEXOR®-system. The nitrogen container for cooling experiments is located on the left side of the instrument. The EPLEXOR®-system itself contains the dynamic vibrator system with strain sensor, the static servo drive, the temperature chamber with thermocouples, the exchangeable force transducers as well as the power supply, amplifiers and the heart of the system, a 32-bit realtime multitasking processing computer.

Figure 3: EPLEXOR® 500 N High End

A schematic view of the system is shown in figure 4. The servo drive unit equipped with a static elongation transducer is located on top of the system. The load cell below the static drive is directly connected with the test specimen. Individual sample holders for different test modes are available. The upper part of the sample is connected with the dynamic shaker system. This dynamic drive is equipped with the second dynamic strain sensor located at the bottom of the system.

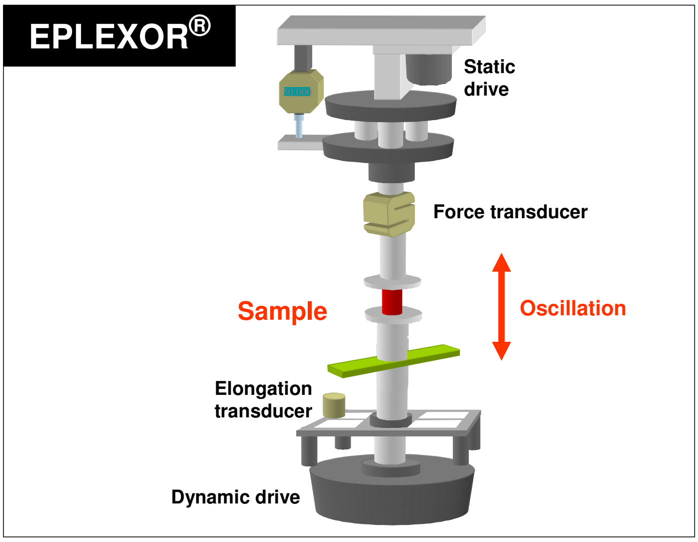

Figure 4 : working principle of the EPLEXOR®-system

Temperature dependence of butyl-rubber (BR) and SBR 1500

All temperature sweeps are performed with a static deformation of 4% strain related to the intial sample length (10 mm for all samples) within a temperature range from –80 ℃ up to 80 ℃. The applied dynamic strain amplitude is +/- 0,2 %. Test frequency is 10 Hz.

Figure 5 shows the complex modulus of a filled (50 phr carbon black) and a unfilled BR in function of the temperature. Due to the carbon black content the modulus of the filled BR is at temperatures above 0℃ about 10 times larger compared to the pure BR.

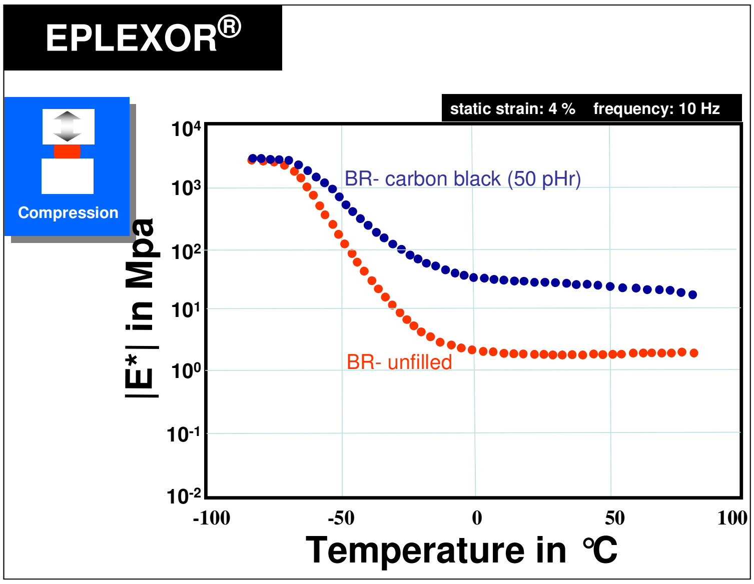

Figure 5 : **Complex modulus |E*| of a filled and unfilled BR-system in function of temperature (comparison)**

The filled as well as the unfilled BR system (figure 6) exhibit a very broad glass transition area covering a temperature range of about 50℃ (half width of tan delta peak). Nevertheless, the tan delta peak values of both systems are quite different (Filled: tan delta peak maximum is 0.75, unfilled: tan delta peak maximum is 1.3)

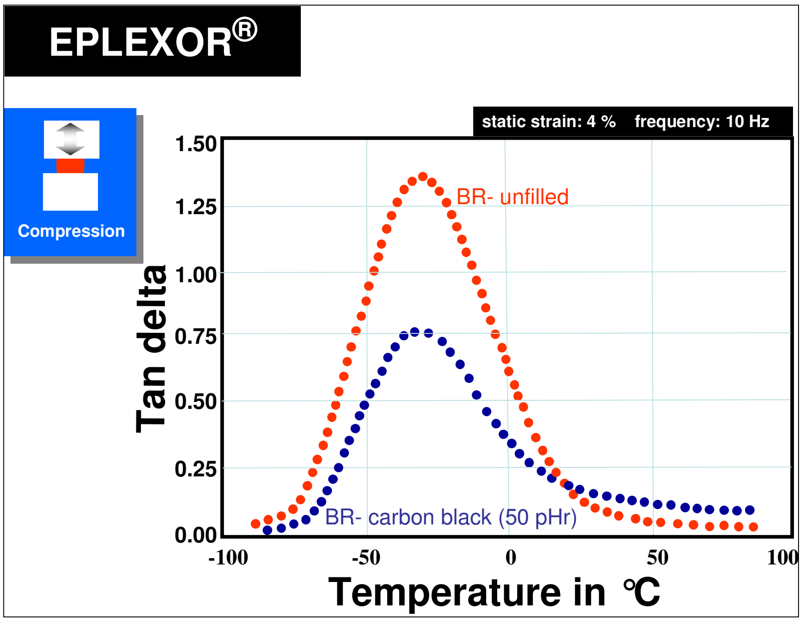

Figure 6 : **tan δ of a filled and unfilled BR-system in function of temperature (comparison)**

Figure 7 and 8 show the complex modulus and tan δ of the second system:
As before a filled and unfilled SBR 1500 system are characterized. The pure SBR shows a very small glass-transition peak compared to the BR system. The half-width value of this Tg transition is only 20 ℃. As before the storage modulus E` of the unfilled SBR decreases from nearly 3000 MPa below Tg to values below 5 MPa above Tg. |E*| of the filled systems is at temperatures above Tg 2 times larger compared with the unfilled SBR 1500.

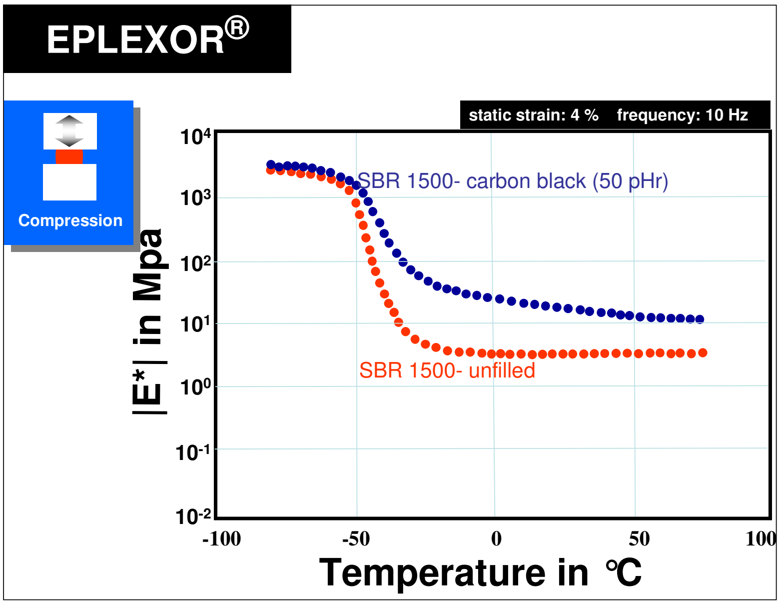

Figure 7: **Complex modulus |E*| of a filled and an unfilled SBR 1500 system in function of temperature (comparison)**

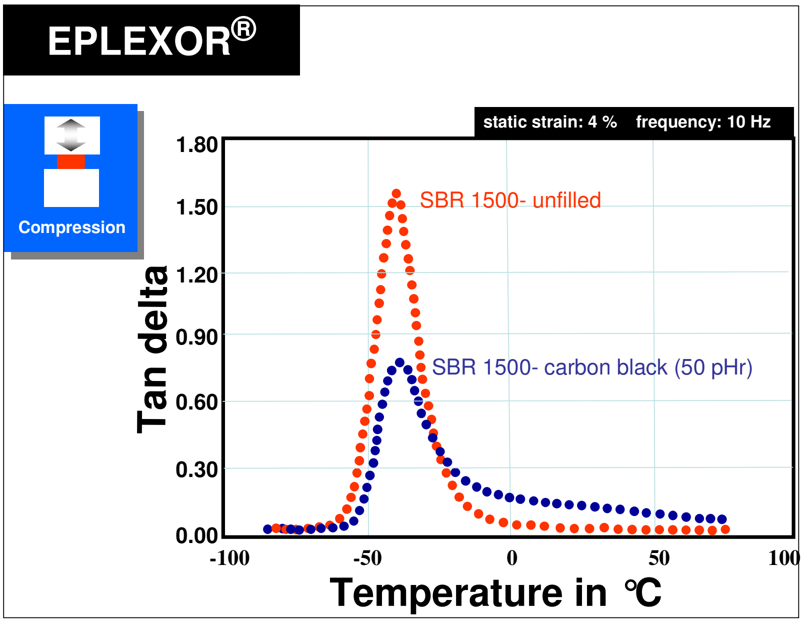

Figure 8 : **tan δ of a filled and unfilled SBR 1500 system in function of temperature (comparison)**

Temperature sweeps allow to distinguish different materials. Unfortunately this is a quite time consuming test.

New fast and intelligent tests showing differences of materials -like a “fingerprint” - will help to reduce the duration of testing.

As a useful technique **frequency** sweeps performed in the glass-transition region are used. Even in this region **DMTA** is working like a **magnifiying glass**.

Frequency sweeps performed on filled and unfilled rubber-systems

Figure 9 exhibits the frequency dependence of the BR systems. Compared to the unfilled BR system (BR-unfilled at 23°C), E` of the filled system (BR-50 phr at 23°C) is shifted to higher values. The line shapes of the filled (BR-50 phr at 23°C) and unfilled (BR-unfilled at 23°C) BR systems at ambient are very close to each other indicating the same frequency behaviour for the filled and unfilled system.

Within the glass transition region at a temperature of T = -20 °C the situation is quite different.
The unfilled BR shows a much higher slope of the E’ curve with increasing frequency compared to the filled system. This result is expected and can be explained by analyzing the temperature sweeps more in detail.
The Temperature sweeps show (see figure 5):
The lower the amount of carbon black, the lower the modulus E’ at temperatures above Tg (for the unfilled BR system E’ is 10 times lower compared to the filled BR), whereas at temperatures below Tg the E’ of filled an unfilled BR is on the same level.
Consequently, the slopes for both E’ curves of the filled an unfilled BR system must be different in order to reach the same E’ level at temperatures below the glass transition starting from different level of E’ at ambient.
On the other hand, the question how does E’ depend on the carbon black content can be answerd with frequency sweeps performed at contant temperatures. Caused by the prinziple of time temperature or frequency temperature superposition the variation of the frequency on constant temperature level supplies identical informations as can be obtained with temperature sweeps.
Typically a frequency sweep needs about 5 minutes only, which accelerates the test procedure drastically compared to conventional temperature sweeps which run about 2 hours.

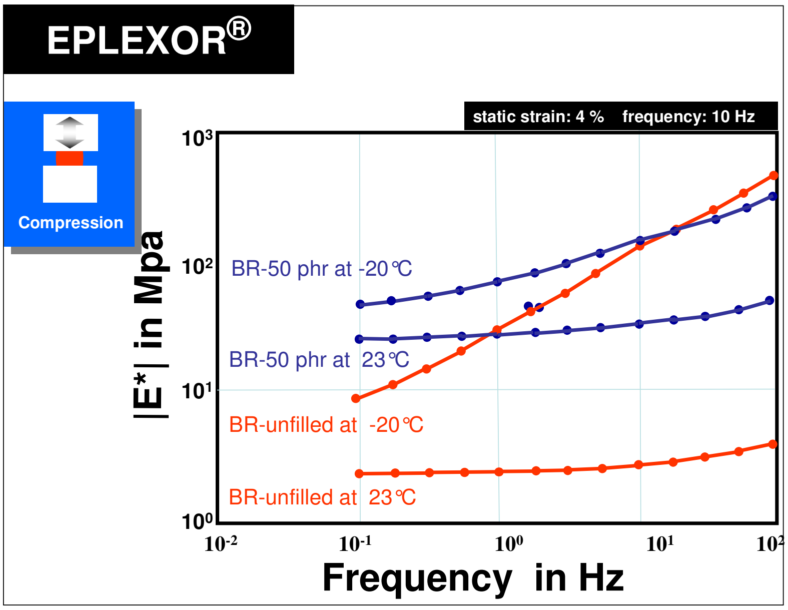

Figure 9 : **Frequency-dependence of filled and unfilled butyl-system (carbon black 50 phr)**

Similar results can be obtained at filled and unfilled SBR 1500 systems (figure 10). As expected, the filled system (SBR 1500 -50 phr at 23°C) generally shows higher values for the storage modulus E' compared to the unfilled one (SBR 1500 -unfilled at 23°C). The slope of both curves does not differ very much at room temperature. Again at –20 °C large differences of the line shape can be recognized which allows distinguishing the degree of filling in by analysis the absolute values of E' as discussed before.

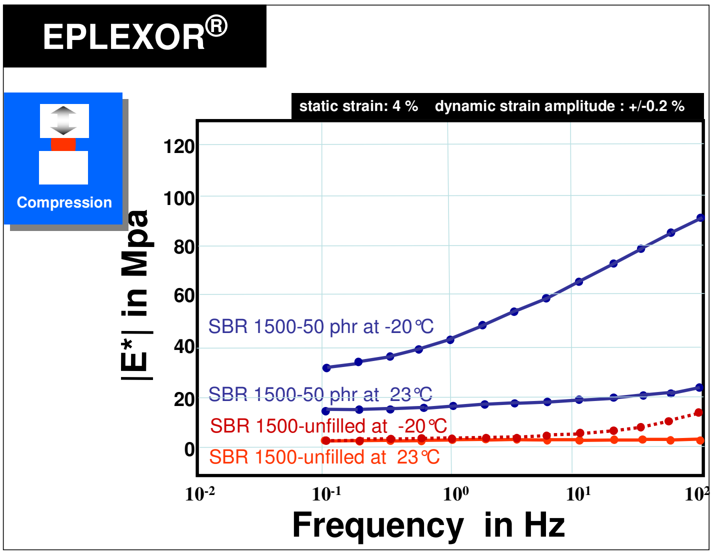

Figure 10 : **Frequency-dependence of filled and unfilled SBR 1500-system (carbon black 50 phr)**

Summary

The test results show frequency sweeps carried out close Tg allows to distingish different levels of carbon black in a quite quick experiment.

The **DMTA** is working like a **magnifying glass**.