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Der Einfluss der Materialzusammensetzung auf die Konstruktion von Masterkurven
The Role of Material Composition in the Construction of Viscoelastic Master Curves

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Introduction

One of the important aspects in the development of new tire compounds is the correlation between the dynamic mechanical properties of the rubber, measured on laboratory scale, and the actual tire performance. In order to predict wet traction, the viscoelastic behavior of the rubber materials at high frequencies (in the megahertz range) needs to be known. Viscoelastic master curves derived from time-temperature superposition can be used to describe the properties of the materials over a wide frequency range.

In this work, the construction of master curves for tread compounds filled with different amounts of silica is discussed. From the vertical shifts as a function of temperature activation energies are derived.

The time-temperature superposition for polymeric materials was proposed by Williams, Landel and Ferry in 1955[1,2] and is generally referred to as the WLF principle. According to this principle, the horizontal shift factor a_T is given by:

$$\log(a_T) = \frac{-C_1(T - T_{ref})}{C_2 + (T - T_{ref})}$$

$$T_g < T < T_g + 100°C \qquad (1)$$

where T is temperature and T_g is the glass transition temperature. The constants C_1 and C_2 vary with the choice of the reference temperature T_{ref}. If T_g +50 °C is taken as T_{ref}, then $C_1 = 8.86$ and $C_2 = 101.6$. These values differ only slightly from one polymer system to the other[2]. The WLF principle has been proven to work well for practical/engineering purposes, for polymers in their molten state, irrespective of whether they are crosslinked or not, as it is based on the free-volume concept[2,3].

If fillers are added to these polymers, and most particularly reinforcing fillers like carbon black and silica, the WLF-principle does not work properly anymore either. Some overlapping of the curves is then seen in the lower frequency range[4-6]. The reason is the additional effect of polymer-filler and even more so filler-filler interactions. The latter is commonly designated as the "filler network", for which the free-volume concept obviously does not apply. The overlapping in the low frequency region (or vice-versa high temperature region) indicates that the filler network dominates here the dynamic mechanical properties of the filler-rubber composite as the rubber matrix is softer[4]. In order to eliminate these overlapping and receive a proper master curve, vertical shifting is necessary.

Experimental

Blends of oil-extended solution styrene-butadiene rubber (S-SBR) and high-cis polybutadiene (BR) with a weight ratio of 70/30 were used in this study. A highly dispersible silica was used as reinforcing filler. The amount of silica was varied between 60 and 80 phr; the compounds are indicated as 37S6, 37S7 and 37S8. In the acronym used, 3 stands for 30 phr of BR and 7 for 70 phr of SSBR. S indicates the silica filler and the last number shows the amount of silica: 6 for 60, 7 for 70 and 8 for 80 phr silica. Dynamic mechanical analyses were performed in the shear and tension mode in a Metravib DMA2000 dynamic spectrometer.

Results

Time-temperature superposition measurements were performed on the compounds. To produce master curves, first a horizontal shift is done along the frequency axis. The WLF equation has been used to calculate the horizontal shift factor a_T according to equation (1). T_g+50 °C and the corresponding universal constants were chosen as reference temperature and C_1 and C_2, respectively. The T_g values for different compounds filled with different amounts of filler were almost the same: −49.5±1 °C. Figure 1 shows the storage modulus after applying the horizontal shifting for the 37S7 sample. In order to obtain a proper master curve, vertical shifts need to be applied. Figure 2 shows the master curves for the loss tangent tanδ of the three different compounds. For the loss tangent tanδ, a crossover is observed; in the high frequency region, the lowest filler loading gives the highest tanδ, but at low frequencies the order is inversed.
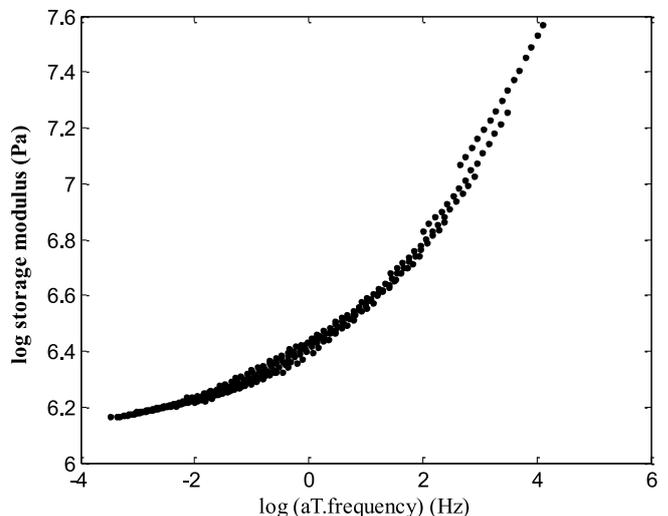

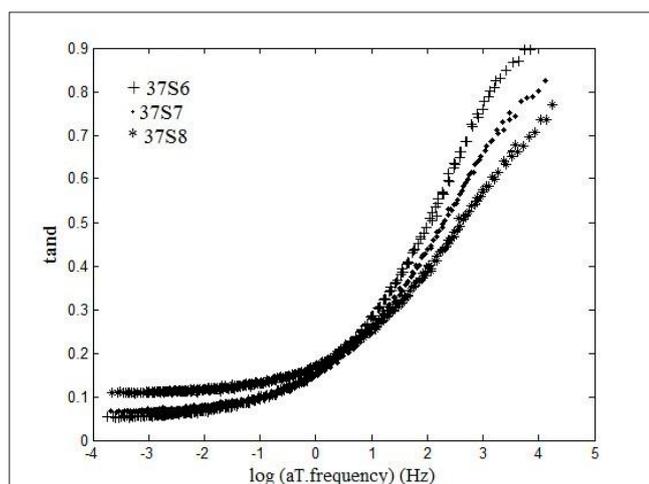**Fig. 1:** Storage modulus for 37S7 after horizontal shifting along the frequency axis, Tref = 0 °C.

Fig. 2: Loss tangent master curve for the different compounds.

In Figure 3, the resulting vertical shift factors for the storage modulus for different samples are plotted versus reciprocal temperature: 1/T. A nearly linear correlation with inverse temperature well above the glass transition temperature is obtained. The slopes of these curves can be interpreted as activation energy of the filler network: Ea. The values of the activation energies for both storage and loss modulus are summarized in Table I.
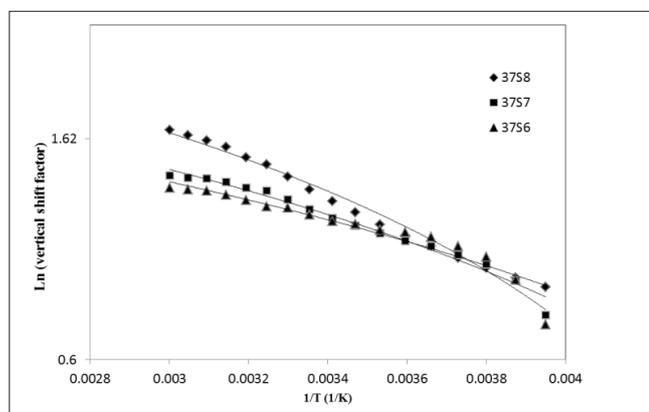

Fig. 3: Vertical shift factor from G' vs. 1/T at temperatures higher than T_{ref}.

	Vertical shift factor	
	Ea (kJ/mol) from G′	Ea (kJ/mol) from G″
37S6	3.3	3.2
37S7	5.4	5
37S8	8	12.1

Tab. 1: Activation energies derived from vertical shift factor measurements for both G' and G"

DISCUSSION AND CONCLUSION

In the high frequency region of the master curve, the loss tangent value decreases with an increase in the amount of filler. It indicates that the presence of filler negatively influences the damping properties of the polymer network. In this region, the transition zone, polymer chains themselves are responsible for the energy dissipation[7]. In the low frequency region, the order of the tanδ values is reversed: the lower the filler content, the lower the tanδ value. At a low frequency, when the polymer is largely outside the transition zone, the major source for energy dissipation is the breakdown and reformation of the filler network. Therefore, a lower tanδ is expected for 37S6 for which the filler network is less developed.

The vertical shift can be considered as a thermally governed process related to the filler particles as they interact with each other (filler network), and as they are connected to the polymer chains (the filler-polymer interaction). The vertical shift factors show Arrhenius type behavior when plotted against 1/T for the high temperature or vice-versa low frequency range of the master curve. Various authors have stated that the activation energy is related to the temperature dependency of glassy shells around the filler particles[4,5,8,9]. In the linear response region, both storage and loss modulus obey the Kramers-Kronig relations[10–12] as the values of the activation energies derived from both are practically the same[4].

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