Superposition approach to the dynamic-mechanical behaviour of reinforced rubbers

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A B S T R A C T

The main goal of present work is to study the dynamic viscoelastic properties of reinforced elastomers with a help of a recently developed superposition approach. To investigate the influence of the filler surface characteristics on the viscoelastic properties, a number of rubber compounds, based on a solution-polymerized styrene butadiene rubber and different types of fillers, was chosen. The master curves for the small strain storage $E'(\omega)$ and loss $E''(\omega)$ moduli were constructed at a reference temperature of $0°C$ with a help of a self-developed shifting procedure based on the time-temperature superposition principle. To fit the master curves for reinforced elastomers in the whole range of frequencies over many decades, we propose to split the polymer matrix into two fractions. One fraction contains the free network chains far away from the filler particles, while the other fraction is composed from the chains localized near and on the filler surface. Such superposition approach allows to extract the characteristics of a fully localized polymer layer with a changed dynamic-mechanical behaviour. Importantly, based on the scaling behaviour of localized layer we show that the surfaces of studied fillers can impose quite different constraints on the rubber chains.

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1. Introduction

The improvement of the dynamic-mechanical properties of the elastomers reinforced with the different fillers like carbon black or silica is of a big interest nowadays. As such rubber nanocomposites are widely used in an auto industry, especially for the tire production, an in-depth study of the dynamic-mechanical properties is strongly required. Thus, it is important to apply recent achievements in the field of polymer physics in order to find approaches with the best description of the dynamic-mechanical behavior of the reinforced elastomers.

The multiscale dynamics of pure rubber networks, randomly cross-linked with different amount of sulfur, has been thoroughly investigated in our earlier work [1]. Four relaxation regimes could be identified from the master curves for small strain storage E' and loss E'' tensile moduli of filled rubbers. These regimes include the classical Rouse-like behavior of Gaussian network strands [2–4] and bending behaviour of semiflexible chain fragments on the length scales shorter than the Kuhn segment [5,6]. Non-polymeric

relaxation processes in a high-frequency regime [7–10] and a low-frequency fingerprint from dangling chain defects [11] comprise a comprehensive dynamic response over 15 decades of frequency.

In the follow-up studies [12,13] the multiscale approach proposed for pure rubber networks has been extended to describe the storage E' and loss E'' moduli of filled rubbers as a function of frequency ω. In particular, the influence of the volume fraction of filler particles on the scaling exponents γ in power-like dependences $E' \sim E'' \sim \omega^\gamma$ for different relaxation regimes was investigated. First of all, in agreement with other studies it was observed that the presence of precipitated silica alters the Rouse-like dynamics of the polymer strands to the slowed down dynamics of chains trapped in the vicinity of the filler surface. The latter dynamics was considered in a series of papers from Vilgis and co-workers [14,15], who predicted the change of scaling exponent 1/2 for pure rubber in the Rouse regime to 3/8 for polymer chains localized on the rough filler surface. To incorporate a gradual change of the scaling exponent from 1/2 to lower values with the increase of the filler loading, we considered a superimposed dynamics in the former Rouse regime [12,13].

Further, in addition to the altered Rouse dynamics, we found a gradual decrease of the scaling exponent in the bending relaxation regime from 3/4 to lower values. For example, the exponent takes a

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value of about 0.4 for the styrene butadiene rubber filled with the high amount (90 parts per hundred rubber, phr) of precipitated silica [12]. This unexpected result is yet difficult to interpret, since there is no prediction in the literature for the change of dynamic behavior of semi-flexible chains in the vicinity of rough surfaces. Therefore, in the previous studies [12,13] of reinforced rubbers we considered the scaling exponent in the bending relaxation regime to be a free fitting parameter. Such extended multiscale approach proved to be very effective for description of the linear dynamic moduli in the styrene butadiene rubbers filled with different amounts of precipitated silica. In particular, it allowed to extract the thickness of the polymer layer localized on the silica surface and to estimate the effective modulus of the filler network; both in dependence on the volume fraction of the filler. On the other side, the multiscale relaxation behaviour of localized chains themselves was not explicitly identified.

To overcome this drawback, in the present study we propose an alternative superposition approach to the dynamic-mechanical behavior of reinforced rubbers and validate it for a wide choice of active fillers. The superposition approach is based on the idea that the polymer matrix in the reinforced rubbers is comprised from two types of polymer chains. One type contains the free network chains far away from the filler particles, while the other type is composed from the chains completely localized on the surface of nanoparticles. Each type contributes to the frequency-dependent moduli in accordance with its fraction in the polymer matrix. A similar idea has been used for example for description of the stress tensor in the analysis of a non-linear viscoelastic behaviour of filled polymer melts [16,17]. In such an analysis, free and localized chains are characterized by a few (non-linear) relaxation modes in the restricted scale range. With our new superposition approach it is a matter of minutes to fit the master curves, both for the storage and loss moduli, in the very wide range of frequencies covering more than 15 decades. An only restriction is that the filler amount should be high enough to cause noticeable changes in network dynamics in a low-frequency region. If it is the case, the fitting parameters allow to predict the dynamic-mechanical behavior of a fully localized polymer network without corresponding measurements. In contrast to our previous approach [12,13], we consider the scaling exponent for the localized chains in the modified Rouse regime to be a free fitting parameter. Interestingly, for some fillers, studied here, this scaling exponent differs from the value 3/8 predicted by Vilgis et al. [15].

The paper is organized as follows. Starting from a description of the materials with a focus on the specification of the surface of each filler, we introduce in Section 2 a shifting algorithm used to construct the master curves and rescaling of the latter on the hydrodynamic reinforcement factor. In Section 3 we demonstrate that the idea of the superposition approach has a strong support from experimental data and also possesses a predictive power. After that we explain how to adapt the description of multiscale dynamics developed for unfilled rubber networks [1] for description of the multiscale dynamics of localized network chains. After presenting essential details of the modeling procedure, we switch to results, which are discussed in Section 4. Here we show that after a successful fitting it is possible to predict a critical volume fraction of the filler, at which complete localization of the polymer matrix takes place.

2. Materials and measurements

Rubber compounds, based on a solution-polymerized styrene butadiene rubber (S-SBR) and different types of fillers, were investigated. The S-SBR with a vinyl content of 50% and a styrene content of 25% (Buna VSL 5025) was provided by Lanxess

(Leverkusen, Germany); its density $\rho_p = 0.95$ g/cm³. As the fillers we used fumed silica with three different surfaces: Aerosil 200 with an unmodified surface, a methylized fumed silica Aerosil R974, and Aerosil 200 Si, with the surface modified by a sulfur containing silane bis (3-triethoxysilylpropyl)-tetrasulfide, Si69); a precipitated silica in three different grades: Ultrasil VN3 untreated, Coupsil 8113 prereacted with Si69 before the mixing process, and Ultrasil VN3 Si reacted with Si69 during the mixing process; and carbon black N330. The chemical composition of the filler surfaces is sketched schematically on Fig. 1. The size of the primary particle is 12 nm for Aerosil, 14 nm for Ultrasil and 28 nm for carbon black. Table 1 shows the recipes of the rubber mixtures. The mixing procedure is described elsewhere [18].

In this study we have used two filler loadings with 20 phr and 40 phr. Samples with 20 and 40 phr were prepared to obtain composites with filler loading lower and above the filler percolation threshold, respectively. In the previous study [18] special attention was taken, not to change the surface energy of the fillers by adding process oils or other dispersion aids. Therefore, a simplified rubber recipe was used, which does not allow mixing of the higher amount of silica based fillers into the matrix (as used i.e. in the rubber industry for tire tread mixtures) with laboratory processing equipment. Nevertheless, as we show below, the filler loading with 40 phr is enough to extract characteristics of a fully localized layer in all studied samples.

The volume fraction of filler particles can be calculated as:

$$\phi = \frac{V_f}{V_f + V_p} = \frac{m_f \rho_p}{m_f \rho_p + m_p \rho_f},$$ (1)

where indexes "f" and "p" refer to the filler and polymer, respectively. As the densities of all fillers are close to $\rho_f \approx 2.0 \pm 0.2$ g/cm³, the two corresponding filler volume fractions are 9% and 16—17% according to Eq. (1).

Linear dynamic-mechanical measurements were performed in the tensile mode with an Eplexor 2000 N dynamic measurement system (Gabo Qualimeter, Ahlden, Germany). The complex tensile modulus, E^*, was measured in the temperature region, T,

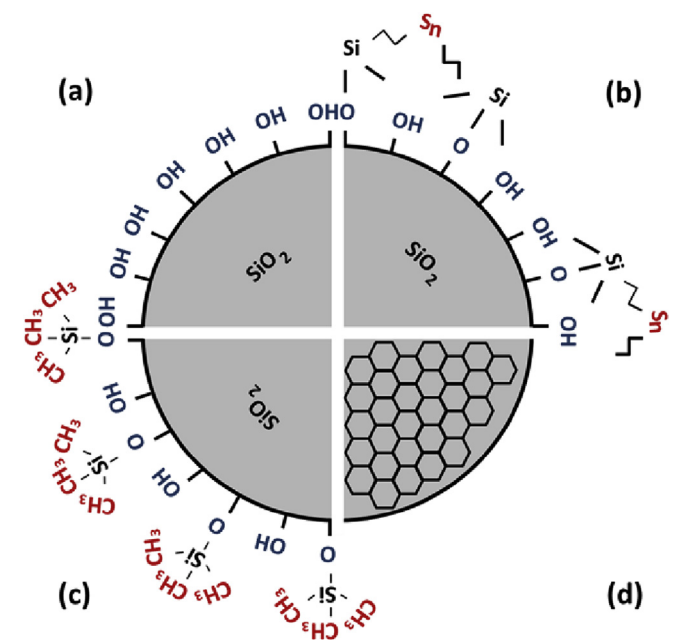**Fig. 1.** Chemical composition of the filler surfaces: Aerosil 200 and Ultrasil VN3 (a), Coupsil 8113 (b), Aerosil R974 (c) and carbon black (d).