



## Depercolation of aggregates upon polymer grafting in simplified industrial nanocomposites studied with dielectric spectroscopy



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### ARTICLE INFO

#### Article history:

Received 8 April 2015

Received in revised form

27 June 2015

Accepted 24 July 2015

Available online 26 July 2015

#### Keywords:

Nanocomposites

Dynamics

Polymer grafting

Percolation

### ABSTRACT

The dynamics of polymer and filler in simplified industrial silica–styrene–butadiene nanocomposites (silica Zeosil 1165 MP, volume fraction 0–21%v) have been studied with broadband dielectric spectroscopy (BDS) and nuclear magnetic resonance (NMR). The fraction of graftable matrix chains was varied from 0 to 100%D3. The introduction of silica nanoparticles is shown to leave the segmental relaxation unaffected, an observation confirmed by the measurement of only a thin (some Angstroms thick) immobilized layer by NMR. The low-frequency measurements are resolved in two distinct dielectric Maxwell–Wagner–Sillars (MWS) processes of different behavior with respect to changes of large-scale silica structures induced by variations of filler fraction and grafting. It is found that increasing grafting leaves the first MWS-process unaffected, while it decreases the strength of the (slower) second MWS by about a decade. At constant silica volume fraction, this indicates depercolation of the filler, thereby providing a microscopic explanation of the evolution of rheological reinforcement. The sensitivity to large-scale reorganizations together with a characterization of local polymer dynamics provides insight over many length- and time-scales into structure and dynamics of nanocomposites, and thus the physical origin of the reinforcement effect.

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### 1. Introduction

Nanocomposites made of nanometric filler particles embedded in a viscoelastic polymer matrix may have outstanding macroscopic properties, among which one can cite mechanical, electrical, or optical ones [1–4]. This broad range makes such systems suitable candidates for applications in very different fields, from car tires to, e.g., biological tissue engineering [5]. Microscopic understanding is necessary if one wishes to tune macroscopic properties of interest, like for instance the optimization of (non-)linear dynamic mechanical properties of car tire material in order to reduce rolling resistance, and thus fuel consumption and CO<sub>2</sub> production. The basis of macroscopic properties is the microstructure, i.e. the dispersion state of the nanoparticles (NPs), which may be

individually dispersed, organized in small aggregates, or form sample-spanning networks of percolated particles or aggregates [6–10]. The microstructure sets the frame for the dynamical properties, which themselves control many macroscopic properties, like, e.g., the time-dependent reaction of samples to mechanical stress which is often based on structural reorganization [11,12].

The local segmental dynamics in nanocomposites has been studied by several groups in the past [13–22]. Polymer in contact with NP surfaces may form immobilized, sometimes referred to as “glassy”, layers which are mainly detected by NMR [13,23]. On larger scales, at high temperature (above the glass transition), the occurrence of a Maxwell–Wagner–Sillars (MWS) process has been reported in several composite systems using broadband dielectric spectroscopy (BDS) [21,24–26]. MWS processes are related to polarization effects due to charge carrier diffusion through the different phases of the nanocomposites. These effects result in the trapping and accumulation of charges at the polymer/silica

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interface. Charges can diffuse on the surface of individual NPs within aggregates, or on a larger scale on the surface of aggregates [27], processes which have been described theoretically by the interlayer model (ILM) [28,29]. The ionic conductivity has also been studied over the whole frequency range [27,30]. In a biphasic material, one may note that the measured conductivity is a global observable, which is related to the polymer, the filler via its surface conductivity, and to the spatial arrangement of the filler which may form conductive pathways of various sizes within the sample.

The dynamical properties of nanocomposites as measured by BDS and NMR have only rarely been compared to macroscopic rheological properties. A correlation has been described in the literature for carbon-black filled elastomers [27,30] and clay nanocomposites [25]. It is unclear, however, if the reinforcement of mechanical properties is dominated by local dynamical heterogeneities bridging NPs [31–33] or large-scale filler structure [34,35]. As far as we know, it is a novelty to study this question using dielectric spectroscopy of silica nanocomposites with multi-scale structure.

Recently, we have contributed to the understanding of the multi-scale structure of silica–styrene–butadiene (SB) simplified industrial nanocomposites using a combination of small-angle scattering, electron microscopy, and numerical simulations [36–39]. Here simplified refers to the absence of any crosslinker and related catalysts. We have built a global model describing structural data where primary silica beads (typical size 17 nm) are organized within small aggregates (typical size 80 nm, aggregation number about 50, giving an internal volume fraction of the order of 35%), which themselves fill large-scale fractal branches (typical width 150 nm). The solid-phase mixing protocol (see SI) applied to industrial silica pellets results in a broad aggregate size distribution of polydispersity 30%. In a first paper focused on dynamics, we have characterized by BDS a new structure-related high-temperature dielectric process termed MWS2, as it occurs in addition to the previously observed MWS process [40]. It takes place across polymer between aggregates as found by an analysis of activation energies [40]. Under  $\Phi_{\text{si}}$  variation which induces aggregate percolation (network formation), a strong increase of the temperature-independent dielectric strength of MWS2 was found around the mechanical percolation threshold of 12%v.

The key question of this second article on dynamics is to understand the relationship between structure and dynamical processes by now varying principally the amount of graftable SB chains (%D3) in order to control the filler structure [37]. Indeed, local dynamics as observed by NMR has been correlated with rheology [32] but the question of the relative importance of large-scale structure with respect to local connections (bridges) through immobilized layers remains open. We therefore focus in the first part of this article on the local scale, and in particular on segmental relaxation investigated by BDS and NMR, as a function of silica content and grafting. Then, the impact of polymer grafting on interfacial dynamics of large-scale silica aggregate depercolation (network destruction) is studied. Finally, both local and large-scale dynamical properties are linked to rheology.

## 2. Experimental section

### 2.1. Materials

Details are given in Refs. [36,37]. The polymer matrix is made of styrene–butadiene random copolymers, with two types of chains of molecular mass 140 kg mol<sup>-1</sup> (PI = 1.07) as determined by size exclusion chromatography. Chains are either linear unmodified SB chains, or bear a single silanol end-function making the chains graftable onto the silica surface by condensation. These

functionalized chains are denoted D3, and the matrix composition is referred to by the percentage of D3 chains (%D3). Both types of chains have been purpose-synthesized by Michelin. The silica pellets (Zeosil 1165 MP from Solvay) have a nominal specific surface of 160 m<sup>2</sup>/g, and the size distribution of the nanoparticles obeys a log-normal law with  $R_0 = 8.55$  nm,  $\sigma = 27\%$  [36]. Nanocomposite formulation is the same as before [36,37] and is detailed in the SI. Real silica volume fractions in nanocomposites have been measured by thermogravimetric analysis (Q500, TA Instruments) and lie in the range  $\Phi_{\text{si}} = 8.4\%v - 21.1\%v$  (i.e., between 21 and 63 phr). The glass-transition temperature was determined using differential scanning calorimetry (Q2000 TMDSC, TA Instruments) in the modulated mode with a heating rate of 3 K/min. For the filled samples,  $T_g$  shows no significant variation with silica content and % D3 as compared to the pure polymer matrix:  $T_g = -37 \pm 0.8$  °C.

### 2.2. Broadband dielectric spectroscopy (BDS)

A broadband high-resolution dielectric spectrometer (Novo-control Alpha) was used to measure the complex dielectric permittivity  $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$  in the frequency range from  $f = 10^{-2}$  to  $10^7$  Hz ( $\omega = 2\pi f$ ) of samples prepared as before [40]. After 20 min equilibration at 60 °C in the BDS cryostat (under nitrogen atmosphere), isothermal frequency measurements have been performed with temperature stability better than 0.1 K. Two series of nanocomposites have been investigated: samples with matrix composition fixed to 50%D3 and  $\Phi_{\text{si}}$  ranging from 8.4 to 21.1%v, and samples with fixed  $\Phi_{\text{si}}$  ( $\approx 8.5\%v$ ) and %D3 varying from 0 to 100%. For all samples, the temperature sequence starts from 333 K down to 153 K. Afterwards, the high-T range between 333 and 363 K has been explored.

#### 2.2.1. BDS fitting

Data treatment was carried out simultaneously on  $\varepsilon'$  and  $\varepsilon''$  using for each temperature the combination of a purely dissipative dc-conductivity term and one Havriliak–Negami (HN) for each dipolar relaxation or MWS process present in the frequency window

$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum_j \frac{\Delta\varepsilon_j}{\left[1 + \left(i\omega\tau_{\text{HN}j}\right)^{\gamma_j}\right]^{\delta_j}} - i \frac{\sigma_{\text{dc}}}{\varepsilon_0\omega} \quad (1)$$

where  $\gamma_j$  and  $\delta_j$  are two shape parameters ranging between 0 and 1, and describing the symmetric and asymmetric broadening of the  $j^{\text{th}}$  process, respectively.  $\Delta\varepsilon_j$  is the dielectric relaxation strength corresponding to the difference between the unrelaxed and relaxed values of the dielectric constant, and  $\tau_{\text{HN}j}$  is the characteristic relaxation time. In our approach, we systematically reduced the number of free parameters in order to extract reliable information, in particular on dielectric strengths and time scales for overlapping processes. A first fit of the data has been performed with all variables let free in the fit function to identify possible trends with temperature for the HN shape parameters. Then, according to the results, these parameters were forced to follow a linear (possibly constant) behavior (see SI).

#### 2.2.2. Dielectric processes

Processes in the neat SB matrix (50%D3) have been investigated, i.e., the  $\alpha$ -relaxation linked to the glass transition and the secondary  $\beta$ -relaxation which has been related to local motions within the butadiene units [41]. In nanocomposites, two additional high-temperature dielectric (MWS1 and MWS2) processes at time scales slower than the  $\alpha$ -relaxation have been identified [40]. The HN parameters for both processes – shape parameters and

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