Study of Filler Structure in Silica Filled SBR compounds by means of SAXS and AFM

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ABSTRACT

The structure of silica particles network in two different solution styrene-butadiene rubbers (S-SBR) was studied by means of small angle x-ray scattering (SAXS) and atomic force microscopy (AFM). S-SBR compounds with different silica contents were analyzed in comparison with their oil extended counterparts. A study into the application of Small-Angle X-Ray Scattering experiments was defined in order to quantify the structures of silica primary particles and clusters in filled rubber compounds up to very high levels of filler content. We propose a modified structure model, which is physically sounder than the widely used Beaucage model and leads to more robust quantification of the silica structures. In addition, an independent characterization of the filler structure was performed by means of AFM. The cluster and particle sizes deduced from both techniques are in close agreement supporting the here proposed approach. The synergetic application of SAXS and AFM allows a consistent and robust characterization of primary particles and clusters in terms of size and structure. These results were compared and discussed in the framework of previously published works.

1. INTRODUCTION

Styrene-butadiene-rubber (SBR) was developed in the 1930s as a replacement for natural rubber (NR) and rapidly became the most produced synthetic rubber. For automobile tires SBR rubbers are often reinforced by the addition of fillers such as carbon black or silica particles¹⁻⁶. In particular, activated silica reinforcement plays an important role in improving the properties of the SBR compounds⁷⁻¹⁰. Moreover, one of the key factors that determine the final properties of these filled compounds is commonly related to the filler structures¹¹. Therefore, understanding the structure of the nanoparticles within the rubber compound becomes of utmost importance from both, scientific and technological point of view. Hence, it is possible to improve both the processability of the compounds and the bulk properties of the final products.

Small-angle scattering and high-resolution microscopy techniques are very suitable for the study of filler morphologies in filled rubber compounds^{3,12-14}. In particular, by combining two independent techniques like atomic force microscopy (AFM) and small-angle X-ray scattering (SAXS), a detailed structural analysis of the silica filled rubbers can be carried out. On one hand, the AFM approach presents the advantage of a real space analysis and, at the same time, the disadvantage of a relatively small experimental 2D spot size, which could restrict the representativeness of the acquired data. On the other hand, SAXS data is highly representative due to the macroscopic sample size that is probed but these data have to be fitted with a suitable model function in order to obtain structural information. Several structural studies in SBR and NR filled compounds have been undertaken by different groups¹⁵⁻²⁰. However, due to the complex hierarchical morphologies associated to the fillers and their diversity of sizes, to date there is no analytical model consistently describing the structure at all length scales.

In 1995, Beaucage proposed a phenomenological model to describe hierarchical structures^{21,22}; however, this model shows some limitations. In order to overcome some of these, the present work proposes a modification of the Beaucage model, which provides physically sound parameters and greater robustness of the fitting procedure. In particular, we focus our study on the structure of precipitated amorphous silica dispersed in industrial solution SBR (S-SBR). Finally, the structural information of the clusters and particles, independently determined by AFM and SAXS, is compared.

2. THEORETICAL BACKGROUND

The filler structure in rubber compounds can be described as a hierarchical structure with several characteristic length scales, as shown in Figure 1. Thus, we have a) primary particles, b) clusters of primary particles (often also called aggregates) and c) larger structures with clusters as basic units, namely: agglomerates.

Figure 1: Scheme of the hierarchical structure in silica filled SBR compounds.

Figure 2 shows the schematic radial averaged scattering for a filled rubber compound, i.e. the scattered intensity $I(q)$ as a function of the modulus of wave vector q . $I(q)$ follows the power-law relationship $I \propto q^{-d}$. The value of the exponent d is directly related to the characteristic fractal dimensions. If $d \leq 3$, the power-law exponent corresponds to the mass fractal dimension d_m , and $d = d_m$. If $3 < d < 4$, the surface fractal dimension, d_s , is related to d as follows: $d = 6 - d_s$. For a smooth surface, d_s is equal to 2 while it takes a value of $d_s = 3$ for infinitely rough surfaces. In this work we consider that the primary particles are represented by spheres with a perfectly smooth surface, symbolized by $d_s = 2$ ²³⁻²⁴. The clusters consisting of primary particles can be described by means of a mass fractal dimension of the cluster, d_m , which corresponds to the compactness and internal structure of the cluster. In the case of a linear, rigid object, this takes a value of $d_m = 1$, whereas in the limit of infinitely compact spherical mass fractals d_m is equal to 3. At this value there is a changeover from mass fractals to surface fractals. In this work we will refer to the power law related to the primary particle as d_p and to the power law related to the cluster as d_{cl} . Therefore, as shown in Figure 2, in the

q -range usually covered by scattering experiments different regimens are observed. The scattering at high q values is mainly determined by the primary particles showing a scattering power law d_p close to -4. The scattering at medium q range is determined by the clusters showing a power law d_{cl} , and at lower q values an additional regime related to the agglomerates is observed. At intermediate q values, a break in the slope may be observed. The position of this break, q_p , is typically related to the average inter-particle distance D_p . In particular, q_p is approximately equal to π/R_p (radius of the primary particle) for nanoparticles in contact. In addition, another break in the slope can be found at even lower q values. In analogy to the primary particles, this second break is close to $q_{cl} = \pi/R_{cl}$ (radius of the cluster). The position of this break, q_{cl} , is typically related to the average inter-cluster distance D_{cl} and separates the cluster regime from the agglomerate regime. Therefore, different scaling regimes may be observed in the scattering diagram. The transition between the different slopes of $d_p \approx -4$ ($d_s=2$) to $d_{cl} = d_m \approx -2.5$ identifies the involved characteristic sizes²⁵. In this context, the measured scattering from the nanocomposites arises from the primary particles and the superstructures they are forming: clusters and agglomerates. Conventional laboratory SAXS measurements cover the q range related to the primary particle and cluster regimes, as shown by the grey area in Figure 2.

Figure 2: Scheme of the experimental radial averaged scattering for a typical filled rubber compound.

2.1 Unified Beaucage Model

One of the most used approaches for the evaluation of the characteristic clusters and particles sizes is the unified model of Beaucage. This model has been often applied for the characterization of the multi-level structure of particles in different systems^{21,22}. In the framework of the Beaucage model the scattering of the system is given by

$$I(q) \cong I_{cl}(q) + I_p(q) \quad (1)$$

where $I_{cl}(q)$ is the scattering contribution from the clusters,

$$I_{cl}(q) \cong H_1 \exp\left(\frac{-q^2 \overline{R_{g,cl}^2}}{3}\right) + H_2 \exp\left(\frac{-q^2 \overline{R_{g,p}^2}}{3}\right) \times \left[\left\langle \frac{\left(\text{erf}(q \overline{R_{g,cl}} / \sqrt{6}) \right)^3}{\overline{R_{g,cl}} q} \right\rangle \right]^{d_{cl}} \quad (2)$$

and $I_p(q)$ is the contribution from the primary particles:

$$I_p(q) \cong H_3 \exp\left(\frac{-q^2 \overline{R_{g,p}^2}}{3}\right) + H_4 \left[\frac{\left(\text{erf}(q \overline{R_{g,p}} / \sqrt{6}) \right)^3}{\overline{R_{g,p}} q} \right]^{d_p} \quad (3)$$

Here, the scattering of the primary particles and the clusters is assumed to be independent from each other, allowing an incoherent sum of both contributions. In addition, each contribution is given by an additive combination of a Guinier law and a term accounting for the scattering in the Porod regime. The fitting parameters of this model are the average radius of gyration of the primary particles $\overline{R_{g,p}}$, its fractal surface dimension of the primary particles d_p , the average cluster radius of gyration $\overline{R_{g,cl}}$ and its mass fractal dimension d_{cl} . In addition, the four pre-factors H_{1-4} are also free fitting parameters. As introduced here, these pre-factors have no distinct physical meaning, however the relationship $H_1 = N_{p,B} H_3$ is often used in the literature, which serves for the estimation of the average number of particles per cluster, $N_{p,B}$ ¹⁹. In total, the Beaucage model has 8 fitting parameters. Therefore, one of the goals of the present work is to propose a new model based on recent developments of the Beaucage Model to reduce the number of parameters and establish a consistent dependence among them. This will help to gain a better understanding of the complex hierarchical morphology of the fillers.

2.2 Modification of the Beaucage Model (MBM)

In this section, we will extend the unified Beaucage model to correlate its free parameters with physical observables characterizing the particle system²⁶. First, for dilute non-interacting single particles, the scattering in the Guinier regime i.e. at $qR_{g,p} < 1$ can be described by the Guinier function:

$$I(q) \cong G_p \exp\left(\frac{-q^2 \langle R_{g,p}^2 \rangle}{3}\right) \quad (4)$$

Compared to equation 3, we include the polydispersity of the system explicitly. The average radius of gyration is given by the relation between the 8th and 6th momentum of the particle radius:

$$\langle R_{g,p}^2 \rangle = \frac{3}{5} \frac{\langle R_p^8 \rangle}{\langle R_p^6 \rangle} \quad (5)$$

In addition, from now on the corresponding pre-factors H_x will be referred as G_p , B_p , G_{cl} and B_{cl} to stress the fact that in the MBM they are no longer independent from each other. By comparing this function with the analytical exact form factor for polydisperse spheres with log-normal distributed sizes, one obtains:

$$G_p = \phi_p \Delta\rho^2 \frac{\langle V_p^2 \rangle}{\langle V_p \rangle} \quad (6)$$

Here, ϕ_p denotes the volume fraction of the particle, $\langle V_p \rangle = \frac{4\pi}{3} \langle R_p^3 \rangle$ and $\langle V_p^2 \rangle = \left(\frac{4\pi}{3}\right)^2 \langle R_p^6 \rangle$

the first and second moment of the average particle volume, and $\Delta\rho^2 = (\rho_p - \rho_0)^2$ the contrast given by the difference in the scattering length density between the particles and the surrounding medium, i.e. the polymer and the other additives. From the definition of the log-normal distribution,

$$f(r) = \frac{1}{r\sigma\sqrt{2\pi}} \exp\left(\frac{\ln(r/R_{av})}{2\sigma^2}\right) \quad (7)$$

the n-th moment of the average radius is the following:

$$\langle R^n \rangle = R_{av}^n \exp\left(\frac{n^2 \sigma^2}{2}\right) \quad (8)$$

Furthermore, assuming a smooth surface of the primary particle ($d_p = 4$, $d_s = 2$), the scattering at high q values, i.e. in the so-called Porod regime, is determined by:

$$I(q \rightarrow \infty) \cong \frac{8\pi^2 \phi_{Si} \Delta \rho^2 \langle S_p \rangle}{\langle V_p \rangle} q^{-4} \quad (9)$$

Here, $\langle S_p \rangle$ is the average surface (proportional to the second moment of the log-normal distribution). By comparison with the leading term of the Beaucage function at high q , we can derive:

$$B_p = 6\pi \phi_p \Delta \rho^2 \frac{\langle R_p^2 \rangle}{\langle R_p^3 \rangle} \quad (10)$$

Combining this information, the form factor of polydisperse particles can be described by:

$$P_p(q) \cong G_p \exp\left(\frac{-q^2 \langle R_{g,p}^2 \rangle}{3}\right) + B_p \left[\frac{\left(\operatorname{erf}\left(\sqrt{q^2 \langle R_{g,p}^2 \rangle / 6}\right)\right)^3}{q} \right]^{d_p} \quad (11)$$

As a last step we include a particle interaction by a virial expansion, as introduced first by Zimm²⁷:

$$I(q) \cong \frac{1}{\frac{1}{P_p(q)} + A_2} \quad (12)$$

Although this shows an extremely rough approximation for as high particle volume fraction as we have, this ansatz can be nevertheless used, since the scattering in the affected q -regime is anyhow dominated by the scattering from the superstructures of the primary particles i.e. the clusters, and this expansion phenomenologically accounts for the reduction of the scattered signal due to the correlation holes arising from the inter-particle correlation within the mentioned clusters.

In the next part, we will extend the model to a second level, which includes the contributions from the aggregated particles, the previously mentioned clusters. In analogy to the primary particles, the scattering contribution at $qR_{g,cl} < 1$ is again dominated by the Guinier term:

$$I(qR_{g,cl} < 1) \cong \phi_p \Delta \rho^2 \frac{\langle V_p^2 \rangle}{\langle V_p \rangle} \overline{N_{p,MBM}} \exp\left(\frac{-q^2 \overline{R_{g,cl}^2}}{3}\right) \quad (13)$$

This expression differs from equation 4 only by a pre-factor $\overline{N_{p,MBM}}$, which is a measure for the average number of particles per cluster, and, of course, the radius of gyration of the particles is replaced by the one of the clusters. As in the Beucauge model, $\overline{R_{g,cl}}$ represents the average cluster radius of gyration. The derivation of the pre-factor in the Porod term of the Beucauge model for the clusters is more complicated. However, with the corrections of Hammouda²⁸ for the pre-factor, one can find:

$$B_{cl} = \frac{\phi_p \Delta \rho^2 d_{cl} \langle V_p \rangle}{(\overline{R_{g,cl}})^{d_{cl}}} \left(\frac{6d_{cl}^2}{(2+d_{cl})(2+2d_{cl})} \right) \overline{N_{p,MBM}} \quad (14)$$

Therefore, the scattering contribution from the cluster is accounted via:

$$I_{cl}(q) \cong G_{cl} \exp\left(\frac{-q^2 \overline{R_{g,cl}^2}}{3}\right) + B_{cl} \exp\left(\frac{-q^2 \langle R_{g,p}^2 \rangle}{3}\right) \left[\frac{\left(\operatorname{erf}\left(\sqrt{q^2 \overline{R_{g,cl}^2} / 6} \right) \right)^3}{q} \right]^{d_{cl}} \quad (15)$$

Here, the additional exponential expression takes the vanishing contributions from the clusters below $qR_{g,p} > 1$ into account. To summarize, the total scattering in the observed q-regime can be approximated by the modified Beaucage model, which has seven fitting parameters:

$$I(q) \cong I_{cl}(q) + \frac{1}{\frac{1}{P_p(q)} + A_2} \quad (16)$$

In addition to the reduction of free fitting parameters, the presented modified Beaucage model has further advantages. First, we introduced an additional term to account for the inter-particle correlations; this especially improves the fitting in the cross-over region. Moreover, the number of particles per cluster can be determined more precisely due to the clear separation of both contributions, from the particles and clusters (this point will be further discussed in section 4.3). Second, the structure of the original Beaucage model is such that there are four terms which can contribute to the scattering intensity in a somewhat arbitrary way, controlled by the parameters H_x . A physical interpretation is done only after the actual fitting, where some system characteristics are derived from their adjusted values and which may lead to unphysical combinations of H_x . Contrary to that, the here-proposed modified model intrinsically introduces the physical dependencies and leads to a coupling of the four terms. Thereby, unphysical fit results are hindered and a more stable fitting process is obtained.

3. EXPERIMENTAL ANALYSIS

3.1 Materials

Two different solution styrene-butadiene rubbers, labeled S-SBR and S-SBR-o were studied in this work. The S-SBR-o was pre-mixed with 37.55 phr (per hundred rubber, parts in weight per 100 parts of rubber) of extender treated distillate aromatic extracts (TDAE oil). S-SBR composition (in weight %) is 25% styrene, 50% 1–2 vinyl, 15.4% 1–4 trans, and 9.6% 1–4 cis, co-monomer distribution. On the other hand, SSBR-o is a random copolymer with 25% styrene, 47% 1–2 vinyl, 17.0% 1–4 trans, and 11.0% 1–4 cis. Amorphous silica (Z1165 MP-Rhodia) with a specific surface area S_{sp} of 165.8 m²/gr was employed as filler. Samples with five different volume fractions (0, 15, 30, 70 and 90 phr) were prepared using Bis-3triethoxysilylpropyldisulfide (TESPD) as coupling agent. The sample labels show the filler content and the oil and non-oil extension respectively. A detailed sample composition is

shown in Table 1, where the antioxidant is [N-(1,3)-dimethylbutyl-N'-phenylp-phenylenediamine], the accelerator is [N-cyclohexyl-2-benzothiazolesulfeneamide] and the secondary accelerator is diphenylguanidine (DPG). The mixing process of rubber, filler, and additives was performed in an internal mixer (the mixing time was kept constant). For all the compounds 15×15 cm square sheet samples (thickness of about 0.7 mm) were then obtained by compression-molding vulcanization (170°C for 10 min).

Table 1: S-SBR/S-SBR-o samples composition

	Unfilled		15phr		30phr		50phr		70phr		90phr	
Rubber (S-SBR / S-SBR-o)	100	137.5	100	137.5	100	137.5	100	137.5	100	137.5	100	137.5
Filler	-	-	15	15	30	30	50	50	70	70	90	90
Coupling agent	-	-	1.2	1.2	2.4	2.4	4	4	5.6	5.6	7.2	7.2
Antioxidant	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Stearic Acid	3	3	3	3	3	3	3	3	3	3	3	3
TDAE oil	15	*	15	*	15	*	15	*	15	*	15	*
Antioxidant 2	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75
Zinc Oxide	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Accelerator	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Secondary accelerator	-	-	0.75	0.75	1	1	1.3	1.3	1.7	1.7	2	2

All quantities are given in phr (parts in weight per 100 parts of rubber).

3.2 SAXS setup

The SAXS experiments were conducted on a Rigaku 3-pinhole PSAXS-L equipment operating at 45 kV and 0.88 mA. The MicroMax-002 X-Ray Generator System is composed by a microfocus sealed tube source module and an integrated X-Ray generator unit which produces CuK α transition photons of wavelength $\lambda = 1.54$ nm. The flight path and the sample chamber in this equipment are under vacuum. The scattered X-Rays are detected on a two-dimensional multi-wire X-Ray Detector (Gabriel design, 2D-200X). This gas-filled proportional type detector offers a 200mm diameter active area with approximately 200 micron resolution. The azimuthally averaged scattered intensities were obtained as a function of momentum transfer $q = (4\pi/\lambda)/\sin\theta$, where θ is half the scattering angle. Reciprocal space calibration was done using silver behenate as standard. Measurements were performed at room temperature with a sample to detector distance of 2 m. The data were background

corrected by subtracting the result of a measurement on the unfilled sample applying the proper transmission corrections.

3.3 AFM setup

Silica filled SBR samples of 200 μm thickness were obtained using a microtome. The filler structures were characterized by using an atomic force microscope Bruker Multimode 8. Moderate/hard ($A_{sp}/A_0 = 0.6/0.5$, where A_{sp} is the set point amplitude and A_0 is the free oscillation amplitude) or soft ($A_{sp}/A_0 = 0.1$) tapping images in air were obtained by using RTESP7 or HMX-10 probes. Nominal values (manufacturer) for the natural frequency, tip radius and cantilever spring constant of RTESP7 probes are $f_0 = 250\text{-}336\text{ kHz}$, $R = 8\text{ nm}$ and $k = 20\text{-}80\text{ N/m}$, respectively. A mechanical characterization of the materials at the nanoscale was performed by using HarmoniX AFM imaging²⁹⁻³¹. HarmoniX can provide simultaneous information about various mechanical aspects of the sample, like peak force, modulus, and surface adhesion, to name a few. For these measurements, specifically designed torsional harmonic cantilevers were employed (previously mentioned HMX-10). The nominal values (manufacturer) for the natural frequency, tip radius and cantilever spring constant for these probes are $f_0 = 70\text{ kHz}$, $R = 10\text{ nm}$ and $k = 1.5\text{-}6\text{ N/m}$, respectively. The acquired images were processed by using WSxM software³².

3.4 AFM analysis: Determination of the surface silica structures filled compounds

Figure 3 shows AFM topography and phase images (soft tapping) of typical filler structures observed in several areas of S-SBR samples. Although there is a clear correlation between the presence of silica clusters and topographic features, no detailed information about the cluster structure can be obtained through this channel. Mechanical phase, on the other hand, does provide a very good contrast between silica and rubber, which in turn allows a precise detection of the different structures. As shown in Figure 3.b and Figure 3.h, there is a rather homogeneous filler distribution along the rubber matrix, independently of the formulation. Typical clusters can be observed in more detail at higher zoom levels, as shown in Figure 3.f and Figure 3.l. At first sight, there are no remarkable differences between clusters in S-SBR or in S-SBR-o compounds. A detailed statistical analysis is performed in Appendix I.

Figure 3: Typical filler structures of S-SBR and S-SBR-o with 50 phr observed by soft tapping acquired at different zoom levels (topography and phase images, respectively). *S-SBR-o*: a) and b) 5 μm ; c) and d) 1 μm ; e) and f) 330 nm. *S-SBR*: g) and h) 5 μm ; i) and j) 1 μm ; k) and l) 330 nm.

4 RESULTS & DISCUSSION

4.1 AFM

Table 2 summarizes the cluster size obtained by means of AFM experiments. In this case, $\langle R_i \rangle$ stands for the apparent radius obtained directly from the AFM images. On the other hand, $\langle R \rangle$ stands for the corrected radius (obtained by taking into account the cutting effect and the method limitations), while σ and $\langle R_{Cl}^{AFM} \rangle$ represent the standard deviation and the average radius obtained from the log-normal distribution (according to the 1st moment of Equation 8). For a detailed discussion of the statistical analysis see Appendix I.

Table 2: AFM size distribution results.

S-SBR / S-SBR-o	$\langle R_i \rangle$ [nm]		σ		$\langle R \rangle$ [nm]		$\langle R_{Cl}^{AFM} \rangle$ [nm]	
15 phr	36	37	0.36	0.22	46	47	49	48
30 phr	30	30	0.4	0.42	38	38	41	42
50 phr	25	28	0.44	0.35	32	36	35	38
70 phr	21	24	0.48	0.51	27	31	30	35

As shown, $\langle R_i \rangle$ decreases with increasing silica volume fraction for both formulations. At the same time, a systematic increment of σ is also observed. Therefore, $\langle R_{Cl}^{AFM} \rangle$ decreases monotonically with increasing silica content. Figure 4 shows $\langle R_{Cl}^{AFM} \rangle$ as a function of silica volume fraction, where this tendency can be easily observed. Recent works show that this tendency can be related to the mixing procedure^{19,20}. As silica content increases, typical cluster distances decrease, in turn increasing compound viscosity and therefore shear forces, breaking up the aggregates into smaller pieces. Within error bars, cluster sizes are nearly the same for both formulations along the analyzed concentration range.

Figure 4: $\langle R_{Cl}^{AFM} \rangle$ as a function of the silica content (volume fraction) obtained through AFM measurements.

4.2 SAXS

4.2.1 Beaucage analysis

In a first step to extract constitutive parameters, the scattering diagrams were fitted by the unified model of Beaucage described in section 2. As shown in Figure 5, the fitted model follows closely the scattering experimental results.

Figure 5: Scattering data and the corresponding Beaucage fitting for S-SBR (above) and S-SBR-o (below) compounds. Symbols stand for the experimental results and lines for the fittings (■ 15phr. ■ 30phr. ■ 50phr. ■ 70phr. ■ 90phr).

According to the specific surface area $S_{sp} = 165.8 \text{ m}^2/\text{g}$, the radius of the particle can be calculated from the relation $\overline{R_p} = 3/(S_{sp}\rho) = 11.1 \text{ nm}$, assuming $\rho = 2 \text{ g/cm}^3$ for the density of the silica particles. Considering these particles as homogeneous spheres, the radius $\overline{R_p}$ can be related with the radius of gyration $\overline{R_{g,p}}$ through $\overline{R_p}^2 = 5/3\overline{R_{g,p}}^2$. As the fittings with the Beaucage model are not stable when using $\overline{R_{g,p}}$ as a free parameter, taking into account the previous assumptions, the radius of gyration of the primary particle was fixed to $\overline{R_{g,p}} = 8.6 \text{ nm}$.

In addition, the value of $\overline{R_{g,cl}}$ was obtained as a free parameter from the corresponding fitting. A general expression to estimate $\overline{R_{cl}}$ from $\overline{R_{g,cl}}$ is written below (assuming the clusters as spherically isotropic mass fractal structures³³)

$$\overline{R_{cl}}^2 = \left(\frac{d_{cl} + 2}{d_{cl}} \right) \overline{R_{g,cl}}^2 \quad (17)$$

where d_{cl} is the corresponding mass fractal dimension of the cluster. As we mention in section 2, if infinitely compact spherical mass fractals are considered, then $d_{cl} = 3$ and a particularization of this equation is obtained ($\overline{R_{cl}}^2 = 5/3\overline{R_{g,cl}}^2$). $\overline{R_{cl}}$ calculated from the equation 17 is presented in Table 4. For the S-SBR compounds the values for $\overline{R_{cl}}$ range from 23.2 up to 30.5nm. However, fitting of the oil extended materials yielded much larger values (ranging from 43.2 to 54.3 nm). Concerning the cluster description, the fit provides a mass fractal dimension, d_{cl} , which is independent of filler concentration. All these results are summarized in Table 3 and Table 4.

Table 3: Structural parameters fitted with the Beaucage model for the X-ray measurements on the silica-filled samples.

		Fixed Parameters		Fitting Parameters					
Sample	Φ (vol%)	$\overline{R_{g,p}}$ [nm]	d_p	H_1	H_2	H_3	H_4	$\overline{R_{g,cl}}$ [nm]	d_{cl}
S-SBR30phr	10.3	8.6	4	11163	26136	820	4964	22.3	2.4
S-SBR50phr	15.9	8.6	4	16222	24560	1535	7641	20.8	2.4
S-SBR70phr	20.7	8.6	4	14527	14189	1900	12578	18.1	2.3
S-SBR90phr	24.9	8.6	4	13431	7898	2507	14269	17.0	2.3
S-SBR-o15phr	4.7	8.6	4	917	3268	32	169	39.7	2.3
S-SBR-o30phr	8.9	8.6	4	1414	5962	55	396	37.6	2.3
S-SBR-o50phr	13.9	8.6	4	1944	7828	93	554	35.3	2.3
S-SBR-o70phr	18.2	8.6	4	2157	10264	133	802	33.0	2.3
S-SBR-o90phr	22.0	8.6	4	2563	11144	170	119	31.6	2.3

Although the statistic description of the experimental curves is rather good, the obtained results do not agree with those observed by using AFM. In particular, S-SBR-o cluster sizes are apparently overestimated by the Beaucage model. Moreover, the aggregation numbers, calculated as $N_{p,B}=H_1/H_3$ and shown in **Table 4**, are lower in comparison with the literature reported values for similar systems^{15,19,20}. The main reason could be related to the fact that the pre-factors H_{1-4} are not correlated among each other. However, from scattering theory, they should be intrinsically correlated to have a physical meaning. In the MBM, we use these dependencies to stabilize the fitting (see section 2).

Table 4: Calculated quantities from the fitted Beaucage model parameters.

Sample	Φ (vol%)	$\overline{R_{cl}}$ [nm]	$N_{p,B}$ $=H_1/H_3$	$N_{p,R_t} = \left(\frac{\overline{R_{g,cl}}}{\overline{R_{g,p}}} \right)^{d_{cl}}$
S-SBR30phr	10.3	30.5	13.4	11.0
S-SBR50phr	15.9	28.4	10.4	9.3
S-SBR70phr	20.7	24.7	7.6	6.7
S-SBR90phr	24.9	23.2	5.4	4.3
S-SBR-o15phr	4.7	54.3	28.6	29.6
S-SBR-o30phr	8.9	51.4	25.7	26.1
S-SBR-o50phr	13.9	48.3	20.9	22.6
S-SBR-o70phr	18.2	45.1	16.2	19.3
S-SBR-o90phr	22.0	43.2	15.0	17.5

4.2.2 MBM analysis

Figure 6 displays the experimental SAXS scattering diagrams of silica filled styrene butadiene rubbers and the corresponding fits with the MBM. In order to obtain physical values of the cluster size from the MBM fitting, we constrained the possible high and low $\overline{R_{cl}}$ limits: a) the average inter-particle distance of 20 nm, obtained from D_p values ranging from 18.5 to 22 nm ($D_p = 2\pi/q_p$), is considered as the low cluster size limit (where q_p is obtained from the break in the scattering diagram slope, as explained in section 2) and b) a rough estimation of the upper $\overline{R_{cl}}$ fitting constraint ($\overline{R_{cl}}=100$ nm) was performed from independent krakty plots (not shown). The obtained fitting parameters, specifying the nature and architecture of the filler, are summarized in Table 5 for all investigated samples. The fitting with MBM is more stable than that with the unified Beaucage model. This is because the Beaucage model allows several combinations of the H_1 , H_2 , H_3 and H_4 values to describe the experimental curves whereas the corresponding parameters are physically coupled.

Figure 6: Scattering data and MBM fitting for S-SBR (above) and S-SBR-o (below) compounds. Lines stand for the fittings and symbols for the experimental data (■ 15phr. ■ 30phr. ■ 50phr. ■ 70phr. ■ 90phr).

As mentioned above, we assume a log-normal distribution of the primary particles size (equation 7), described by R_{av} and σ^{34} . In this context, the average radius of the primary particle $\langle R_p \rangle$ is given by equation 8. Within error bars, the average primary particle radius $\langle R_p \rangle$ is constant for all studied compounds (see Figure 7 and Table 6) and, therefore, an average radius across all compounds of $\overline{\langle R_p \rangle} = 6.63 \pm 0.18$ nm can be calculated. Concerning the cluster description, the fit provides the cluster radius of gyration $\overline{R_{g,cl}}$, the mass fractal dimension of the cluster d_{cl} and the number of particles per cluster or aggregation number $\overline{N_{p,MBM}}$ (see Table 5).

Table 5: Structural parameters fitted with the MBM approach for the X-ray measurements on the silica-filled samples.

	Fixed		Fitting Parameters					
Sample	Φ_{Si} (vol%)	d_p	$R_{p, av}$ [nm]	σ	A_2	$\overline{R_{g,cl}}$ [nm]	d_{cl}	$\overline{N_{p,MBM}}$
S-SBR30phr	10.3	4	6.90 ± 0.39	0.103 ± 0.004	0.075 ± 0.007	33.2 ± 3.2	2.28 ± 0.05	32.5 ± 5.0
S-SBR50phr	15.9	4	6.54 ± 0.47	0.122 ± 0.005	0.061 ± 0.009	29.9 ± 3.6	2.26 ± 0.05	28.2 ± 6.6
S-SBR70phr	20.7	4	6.73 ± 0.58	0.119 ± 0.005	0.038 ± 0.014	24.8 ± 3.0	2.32 ± 0.05	17.0 ± 4.4
S-SBR90phr	24.9	4	6.63 ± 0.54	0.108 ± 0.007	0.042 ± 0.011	21.0 ± 3.9	2.31 ± 0.05	12.0 ± 5.5
S-SBR-o15phr	4.7	4	6.39 ± 0.61	0.171 ± 0.007	0.135 ± 0.031	39.8 ± 5.9	2.31 ± 0.07	45.5 ± 4.4
S-SBR-o30phr	8.9	4	6.78 ± 0.78	0.092 ± 0.009	0.010 ± 0.006	36.6 ± 4.3	2.42 ± 0.09	38.9 ± 7.1
S-SBR-o50phr	13.9	4	6.39 ± 0.63	0.103 ± 0.013	0.097 ± 0.011	32.4 ± 4.8	2.43 ± 0.08	35.1 ± 8.1
S-SBR-o70phr	18.2	4	6.52 ± 0.75	0.100 ± 0.012	0.062 ± 0.008	29.9 ± 5.1	2.42 ± 0.09	31.0 ± 8.9
S-SBR-o90phr	22.0	4	6.77 ± 0.85	0.102 ± 0.014	0.044 ± 0.009	27.7 ± 4.3	2.40 ± 0.08	25.4 ± 7.5

As explained before, we consider the clusters as spherically isotropic fractal structures. Therefore, the radius of the cluster $\overline{R_{cl}}$ can be determined according to equation 17. As depicted in Figure 7 (see also Table 6), the obtained $\overline{R_{cl}}$ decreases as the filler fraction increases. In addition, for a given rubber type, d_{cl} does not change with the filler concentration. However, systematic differences (about 10%) can be observed for S-SBR and S-SBR-o. While an average value of about 2.3 is obtained for S-SBR compounds, S-SBR-o compounds show a value of about 2.4. As explained above (see section 2), d_{cl} is related with the fractal distribution of the primary particle inside the clusters, i.e. with the cluster compactness. According to the d_{cl} definition, the MBM reveals more compact silica clusters in the oil extended compounds.

Table 6: Calculated quantities from the fitted MBM parameters.

Sample	Φ_{Si} (vol%)	$\langle R_p \rangle$ [nm]	$\overline{R_{cl}}$ [nm]	$N_{p,R_g} = \left(\frac{\overline{R_{g,cl}}}{\overline{R_{g,p}}} \right)^{d_{cl}}$
S-SBR30phr	10.3	6.93	45.4	35.6
S-SBR50phr	15.9	6.60	40.9	30.4
S-SBR70phr	20.7	6.77	33.9	20.3
S-SBR90phr	24.9	6.67	28.4	11.1
S-SBR-o15phr	4.7	6.48	54.9	66.2
S-SBR-o30phr	8.9	6.81	49.5	58.5
S-SBR-o50phr	13.9	6.43	43.9	50.9
S-SBR-o70phr	18.2	6.55	40.5	39.4
S-SBR-o90phr	22.0	6.81	37.5	29.0

The aggregation number is obtained from MBM fitting ($\overline{N_{p,MBM}}$) as well. Figure 7b shows the results for S-SBR and S-SBR-o compounds as a function of silica volume fraction. In particular, the differences between compounds are more pronounced in the $\overline{N_{p,MBM}}$ representation. An alternative way to calculate the aggregation number, depending on R_{cl} and d_{cl} , can be found in the literature ²⁶:

$$N_{p,R_g} = \left(\frac{\overline{R_{g,cl}}}{\overline{R_{g,p}}} \right)^{d_{cl}} \quad (18)$$

Specifically, equation 18 shows that a higher N_{p,R_g} value in S-SBR-o is related to a higher compactness as well as to a higher $\overline{R_{g,cl}}$. Therefore, the combination of a slightly higher $\overline{R_{g,cl}}$ and a higher d_{cl} for S-SBR-o explains the differences compared to S-SBR. In this context, the results of N_{p,R_g} (Table 6) are in good agreement with the $\overline{N_{p,MBM}}$ values obtained from the MBM fittings for S-SBR compounds, but are higher for S-SBR-o.

Figure 7: a) $\overline{R}_{cl}$ as a function of silica content for S-SBR and S-SBR-o compounds. Inset: $\langle R_p \rangle$ as a function of silica content. b) $N_{p,MBM}$ as a function of silica content.

4.3 Rationalization of the results.

In this work, the silica structure in the rubber compounds has been studied by using two independent approaches, AFM and SAXS. It is shown that, despite their limitations, the combination of these complementary techniques can be used in a synergetic manner to establish a robust characterization of silica structures in rubber compounds.

4.3.1 Structural filler information by SAXS and AFM

As shown in the previous sections, the primary particle size distribution does not depend on the silica content or rubber formulation. The frictional forces that come out during the mixing stage are not able to break them. Moreover, the observed radii are slightly smaller than reported values for similar systems. This difference could be related with the origin of these values; the radius of the primary particle is commonly obtained from the corresponding density and specific surface area $\overline{R}_p = 3/(S_{sp}\rho)^{1/6}$. However, the so-calculated average radius is proportional to the ratio $3^{rd}/2^{nd}$ moment of $\langle R_p^n \rangle$, leading to an overestimation of $\overline{R}_p$. On the contrary, in this work $\langle R_p \rangle$ is directly retrieved from the log-normal distribution parameters (R_{av} and σ) obtained from the MBM fitting. Another important point to be addressed is the fractal dimension of the particles. As shown in section 2.1, one of the MBM assumptions is that $d_p = 4$ ($d_s = 2$, corresponding to a perfectly smooth particle). The agreement between the fittings and the scattering data further support the validity of this assumption.

In the case of the clusters, it is observed that $\overline{R_{cl}^{SAXS}}$ and $\langle R_{cl}^{AFM} \rangle$ decrease as the silica content increases. A possible reason might be the increase of the frictional forces among clusters during the mixing process when increasing the silica content. As silica content increases, the cluster distance decreases (i.e. the clusters interaction increases) in turn increasing the frictional force among clusters and the corresponding breaking process. It is necessary to mention here, that the mixing time was kept constant in order to remove the influence of the mixing procedure. Furthermore, the cluster sizes resulting from SAXS analysis (see Figure 8a) show systematically bigger radii for S-SBR-o compounds compared to their S-SBR counterparts. Higher oil concentrations could be related to lower shear stresses and, therefore, higher cluster sizes. In addition, MBM shows a 10% higher S-SBR-o fractal dimension of the clusters. Accordingly, it can be concluded that the S-SBR-o compounds studied here show more compact clusters than S-SBR. The same $\overline{R_{cl}^{SAXS}}$ trend is also followed by the aggregation number of the compounds which depend on $\overline{R_{g,cl}}$ and d_{cl} . This tendency agrees well with literature results for similar SBR silica systems as discussed in the section below. In addition, a noticeable difference in $\overline{N_p}$ has been obtained between S-SBR and S-SBR-o compounds (see Figure 7). It is found that this value, obtained by using two different methods, is higher for the oil extended compounds. We can conclude that although AFM and SAXS are completely independent approaches, the obtained $\overline{R_{cl}^{SAXS}}$ and $\langle R_{cl}^{AFM} \rangle$ values are in close agreement within the experimental uncertainties. The visible tendency to observe slightly lower radii in AFM than in SAXS may be explained by the fact, that the fitted $\overline{R_{cl}^{SAXS}}$ are a measure derived from higher orders of the cluster sizes, if these are not monodisperse.

Figure 8: MBM and AFM analysis results for: **a)** $\overline{R_{cl}^{SAXS}}$ and $\langle R_{cl}^{AFM} \rangle$ **b)** $\overline{N_{p,MBM}}$ and $N_{p,Rg}$.

4.3.2 Cluster structure in comparison with literature results

In Figure 9, the results from the previous chapters are compared to data from literature. As an example, the average cluster radius is plotted together with the findings from Baeza et al.¹⁵, Schaefer et al.¹⁹ and Schneider et al.²⁰ for similar silica filled rubbers, i.e. SBR based rubbers. The microstructures of the used SBR's are rather different between all literature sources as well as the silica particles are from different suppliers. However, for consistency, only silica fillers with the same specific surface area ($S_{sp} = 120 \text{ m}^2/\text{g}$) are considered here. Despite these differences, the cluster sizes derived in this work are in close agreement with the results from literature. The same trend is observed for the number of particles within a cluster (not shown). This may lead to the conclusion, that the silica itself determines the resulting cluster structures irrespective of the SBR microstructure. Nevertheless, significantly higher cluster sizes are observed for a similar silica dispersed in a polymer of different type, i.e. polyisoprene (PI) as studied by Botti et al.¹⁶.

Figure 9: Comparison of cluster radii from MBM and AFM analysis results with reported results on similar systems.

4.3.3 Evaluation of the modified Beaucage model.

Figure 10 shows the scattering diagram for a 50 phr S-SBR compound. These experimental results ($\square$) were fitted by using the Beaucage (4.2.1) model as well as the MBM (4.2.2). Taking only the overall fitting quality into account, both models give an accurate description of the experimental data. However, a more detailed analysis shows severe differences between both. In Figure 10, a comparison of the modeled scattering contributions from the particle only is plotted. There, one can clearly see that the particle scattering of unmodified Beaucage model dominates in the complete observed q -range (blue line). Therefore, the influence of the fit parameters related to the clusters is underestimated, which should dominate massively below $q \sim 0.025 \text{ \AA}^{-1}$ (see section 4.2.1). As a result, the obtained values for H_3 , H_4 , d_{cl} and $\overline{R}_{cl}^{SAXS}$ are very dependent on the initial guess and not unique. This dominating scattering of the clusters is much more reasssembled by the MBM, leading to a more stable fitting procedure.

Figure 10: Scattering diagram for a 50phr S-SBR compound fitted by using Beaucage and MBM models.

shows the corresponding MBM fitting results, where cluster radii of about 41 nm can be observed. As also shown, cluster radii of about 28 nm are obtained from the Beaucage model for the same experiment. From section 4.1, it is clear that the AFM based approach clearly supports the observed MBM values over their Beaucage counterparts.

6. CONCLUSIONS

The hierarchical structure of silica nanoparticles in two different styrene-butadiene filled rubbers was studied by means of SAXS and AFM. S-SBR compounds with different silica contents were analyzed in comparison with their oil extended counterparts S-SBR-o. SAXS scattering results were analyzed by using two different approaches, the commonly used Beaucage model and a (here) modified version of the later, denoted as MBM. In addition, AFM studies were independently conducted. For those filler levels, where both techniques could be applied, cluster and particle sizes are in close agreement supporting the approach proposed. The results reveal smaller cluster sizes for higher silica contents, in close agreement with literature data for similar systems. In particular, a more compact cluster structure was found by MBM in the oil extended compounds studied here. The present study has shown that the synergetic application of SAXS and AFM allows for getting a consistent robust characterization of primary particles and clusters in terms of size and structure. As one next step, we intend to run SAXS/U-SAXS experiments at a high-brilliance synchrotron facility to extend the characterization towards the scale of filler networks and agglomerates. This would lead to the capability to address all relevant length scales of filler structures beginning from the primary particle up to the agglomerate level in a single experiment.

APPENDIX I

a) Real and apparent radius

Before performing any statistical AFM based analysis, it is worth stressing the differences between the structure of the “real” material, and the observed filler structure in a “material sample”. As AFM samples are prepared by cutting the real material into thin sheets, and images contain information of the surface, there is a distortion in the observed clusters/aggregates sizes.

Figure A1: Scheme of real (R) and apparent radii (R_i) in AFM experiments.

Figure A1 shows a scheme of the observed sizes when obtained from a plane (A-A' in this example) by using AFM. For a given cluster of (real) radius R , the probability of observing an apparent radius R_i depends on the position of this cluster with respect to the A-A' cutting plane. By assuming a large enough number of these structures, every cutting plane becomes equally probable. Therefore, the relationship between AFM observed radius and the real value is defined by the average, $\langle R_i \rangle = \int_0^R \frac{\sqrt{R^2 - r^2}}{R} dr$.

At this point, it is worth noticing that a cluster is not really “cut” during sample preparation, but somewhat “revealed” to different extents by ripping off the polymer above it. This means that there is always some polymer above silica structures affecting the observed size. The amount of “detected” polymer, in turn defining the measured apparent radius, also depends on the imaging parameters (like indenting depth among others). Figure A2 shows some typical

cluster structures in a 15phr S-SBR sample, as observed by soft and moderate tapping. As shown, a detectable layer of polymer can be observed in soft tapping images ($A_{sp}/A_0 < 0.1$) due to the low tip indenting depth. However, as the tapping strength is increased, the hard silica surface below this polymer layer is clearly revealed.

Figure A2: Mechanical phase images of the polymer above silica clusters in a 15 phr S-SBR sample. The experiments were performed by using (from left to right) soft to moderate tapping.

b) Image filtering and particle counting

As already shown, AFM imaging parameters can be appropriately tuned to achieve a rather good contrast between silica structures and rubber. Therefore, a particle count analysis can be performed by phase-filtering (or a filtering with any other available experimental channel, as dissipation or modulus, among others) these images in order to separate particles and aggregates from rubber. In a second step, filtered data can be further processed to obtain a particle count by equivalent disk radius of the observed structures. So obtained data are then plotted as histograms, and fitted with two log normal distributions representing: a) particles, and b) clusters of particles. The apparent cluster average radius, $\langle R_{Cl}^{AFM} \rangle$, is then obtained from equation A1 (first moment of equation 8), after applying the previously mentioned cutting effect correction ($\langle R \rangle = \frac{4}{\pi} \langle R_i \rangle$).

$$\langle R_{Cl}^{AFM} \rangle = \langle R \rangle \exp\left(\frac{\sigma^2}{2}\right) \quad (A1)$$

In the case of particles, the corresponding parameters $\langle R \rangle$ and σ were fixed from previous SAXS fittings (due to the fact that most of these structures are in the limit of the microscope resolution). Therefore, complementary cluster and agglomerates information can be obtained

from standard AFM experiments. A representative image of the above mentioned process is shown in Figure A3.

Figure A3: HMX peak force images of S-SBR-o 50phr. The raw peak force image and the filtered result are presented. Resulting radius histogram is shown below, where blue line stands for the fitting results of log normal distributions (representing particles and clusters).

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