Nanofiller Structure and Reinforcement in Model Silica/Rubber Composites: A Quantitative Correlation Driven by Interfacial Agents

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ABSTRACT: We report a complete analysis of model silica/styrene–butadiene rubber (SBR) nanocomposites including a direct and quantitative correlation between the filler structure and the mechanical reinforcement. We compared two different ways of sample processing: a solvent casting route with well-defined colloidal silica and the manufacturing process of internal mixing with industrial silica powder. The multiscale filler dispersion was characterized with a combination of SAXS/TEM in both reciprocal and direct space. The mechanical properties were determined with oscillatory shear measurements. We evaluated the influence of two polymer-filler interfacial additives on the filler dispersion: a coating agent and a coupling agent for different particle concentrations. Using simple analytical functions, we succeed in modeling the filler dispersion. We obtained surprisingly the same general trend whatever the sample processing, solvent casting, or internal mixing. The primary particles form fractal primary aggregates inside the matrix as a result of a diffusion-limited aggregation process driven by the interfacial additive. The coupling agent, which can form covalent bonds with the matrix chains, leads to smaller and denser primary aggregates while the coating one gives rise to larger and more ramified objects. This can be explained by the restriction of nanoparticle diffusion due to covalent bonds. The primary aggregates arrange into a secondary large scale structure, agglomerates, or by a branched network. The spatial correlations between the primary aggregates follow a Percus–Yevick function allowing us to distinguish between more or less interpenetrated networks in a situation of percolation. The viscoelastic behavior of the composites has been analyzed quantitatively with a percolation model. Below the percolation threshold, the reinforcement is mostly driven by the cluster compactness. We highlight a mechanical percolation whose threshold is dependent on the interfacial additive, but not on the material fabrication process, arising at lower filler volume fraction than the structural percolation. Above the percolation threshold, the network modulus varies as the power three of filler network density, traducing the degree of interpenetration of the aggregates inside the network, is driven by both the interfacial additive and the samples preparation: the coupling agent as well as the internal mixing process gives rise to a denser network with a resulting improved modulus.

1. INTRODUCTION

Polymer nanocomposites are attractive materials due to their outstanding potential applications in a broad range of industrial fields, particularly in tire manufacturing. From a fundamental point of view, it is a real challenge to elucidate the mechanisms that relate the nanoscale structure of the materials with the macroscopic viscoelastic behavior of such complex systems. Presently it is also a challenge for the industry to create innovative and high performance products while reducing fuel consumption and CO₂ emission. Polymer nanocomposites are made by dispersing nanoparticles in a polymer or elastomer matrix and keeping the characteristic scales in the nanometric range. It is commonly admitted that the mechanical properties are related to two main contributions: (i) the filler contribution for which the particles can be organized according to multiscale processes, from the individual dispersion to fractal aggregates more or less ramified, and of variable global size, which results in variable degree of interpenetration and/or connectivity (percolation) to form at a final stage heterogeneous or complex networks; (ii) the polymer chain contribution that involves both perturbation of the chain conformation and dynamics. Different strategies have been performed to tune the filler dispersion in model systems using colloidal filler or in simplified industrial systems using precipitated filler. One can play with the

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sample processing conditions,\textsuperscript{10,11} with the polymer chemical composition\textsuperscript{12–15} and with the electrostatic interactions.\textsuperscript{16} More recent developments have focused on the use of polymer grafted nanofiller, where the particle dispersion can be controlled with the interaction between free and grafted chains.\textsuperscript{17–20} For simplified industrial systems, filler is usually carbon black\textsuperscript{21} or precipitated silica,\textsuperscript{22–27} and the control of the particle dispersion can be achieved with specific interfacial additives. In systems inspired from the tire industry, these additives are coating agents, octyltriethoxysilane (OCTEO), that can covalently bind to the surface of the silica and are known to improve the compatibility with the polymer. Alternatively, the coupling agent sulfur-functional organosilane bis(triethoxysilyl)propyl tetrasulfide TESPT (Si69) has been widely used as one of the key products in tires, significantly improving wet grip and rolling resistance. It can be covalently bonded to both the particles and the matrix chains. The filler dispersions are characterized classically with small-angle scattering techniques (SANS and SAXS) associated with real space images (TEM or AFM)\textsuperscript{28}. Despite powerful advantages, these characterizations remain mostly qualitative\textsuperscript{29} or limited to form factor modeling\textsuperscript{30} when using the Beaucage approach.\textsuperscript{31} Because of the complexity of the systems and especially to polydispersity effects, the transfer from theoretical concepts\textsuperscript{32} and simulations\textsuperscript{33} to quantitative analysis of real experiments is not obvious. As a result, it could be difficult to establish correlations with the mechanical models\textsuperscript{34,35} that usually report the variation of the reinforcement factor as a function of the particle volume fraction. Aggregation indeed modifies strongly the effective volume fraction that can be evaluated only with a precise knowledge of the aggregates’ morphologies. At the same time, aggregates interact at more or less extended distances, which modulate the strength of the resulting network. These interactions and morphologies can be modulated not only with additives which tune the particle–filler interfaces but also by the sample processing conditions. Following the method chosen for sample processing, the aggregation mechanisms can be controlled by the medium viscosity or by the rheological constraints imposed during the mixing process. Because of this combination of effects, the systematic influence of additives as well as the one of the sample processing on the aggregates morphologies and interactions and the resulting consequences on the elastic modulus are still not clearly described.

In the present study we report a complete analysis of silica filler dispersions in styrene–butadiene rubber (SBR) matrix as a function of the particle volume fraction, the nature and the quantity of the additive (a coating agent OCTEO and a coupling agent Si69), and two different routes of sample processing: the solvent casting, which we have associated with well-defined colloidal particles, and the manufacturing process using an internal mixing which we used with industrial precipitated silica. A recent study by Baeza et al.\textsuperscript{36} on similar systems (precipitated silica dispersed in functionalized SBR) prepared with internal mixing showed a quantitative modeling approach of the SAXS from the silica aggregates based on numerical simulations and extrapolation to experimental curves. They proposed a refined self-consistent approach based on the influence of the polydispersity on the interaggregate structure factor, from which they can deduce quantitative parameters on the aggregates morphology and interactions. Here we propose an alternative analytical approach by modeling directly and independently the form factor and the structure factor of the objects which enables then to separate both contributions quantitatively as a function of the experimental conditions. We have identified a hierarchical organization from the native silica particles to the formation of a secondary aggregated large scale structure. The relevant length scale of the system is associated with primary aggregates whose form and structure factors variations can be calculated for all sample processing conditions as well as additive and particle concentrations. This modeling enables a direct quantitative evaluation of a percolation model to reproduce the viscoelastic behavior of the materials.

2. MATERIAL AND METHODS

2.1. Nanocomposites Preparation. 2.1.1. Solvent Casting Systems. The colloidal solution of silica nanoparticles is obtained from Aldrich (Ludox LS colloidal silica, 30 wt % suspension in water). Its specific area is taken as claimed by the supplier: $S_{BET} = 215 \text{ m}^2/\text{g}$. In this solution, the native particles of an average radius of 80 Å are electrostatically dispersed in water. They are transferred to dimethyl-cetamide (DMac) using a solvent transfer protocol described in a previous paper.\textsuperscript{10} DMac is a polar solvent in which primary Ludox particles remain dispersed and is also a good solvent for SBR at high temperature ($130 ^\circ \text{C}$). After solvent transfer and dilution, we use Ludox as 2% v/v suspension in DMac. Dispersing agents OCTEO and Si69 are in a liquid form at room temperature. They are diluted at 7% v/v in methanol (MeOH), and this solution is then introduced in the Ludox–DMac suspension in the nominal quantity of 1 or 2 triethoxysilyl groups per nm$^2$ of silica. The suspension containing Ludox agent is then stirred for 24 h at room temperature. Styrene–butadiene rubber (SBR) is synthesized by Michelin and used as supplied ($M_w = 140 \text{ 000 g/mol, PDI = 1.1}$). Each chain is a statistical copolymer with styrene (26 wt %) and butadiene (74 wt %) units (41% of which is 1–2 and 59% of 1–4). To prevent thermal oxidation of butadiene groups, the bulk polymer contains two antioxidants (AO-2246 and 6-PPD, about 1 wt %), and we work under nitrogen flow. The glass transition temperature $T_g$ of pure SBR was measured by differential scanning calorimetry at around $–35 ^\circ \text{C}$. In a typical run, a 25 mL volume of DMac is previously submitted to a nitrogen flow for 2 h. Then a concentrated solution of SBR in DMac (10% w/w) is obtained by mixing SBR in DMac, stirring using a magnetic rod for 3 h at $130 ^\circ \text{C}$, above the $\Theta$ temperature of the SBR/DMac mixture and largely below the boiling point of DMac ($167 ^\circ \text{C}$). Keeping this temperature, the Ludox suspension with agent is then added slowly at various fractions, ranging from 0 to 16.7% v/v, and stirring is continued at $130 ^\circ \text{C}$ for 1 h. 0.5 aminopropyltriethoxysilane (APTEOS)/nm$^2$ of Ludox is prepared as an additive to the formulation. For OCTEO-treated Ludox, APTEOS is added at the end of the stirring phase Ludox + OCTEO in DMac solution, to prevent silica demixing during the coming casting phase. For Si69-treated Ludox, APTEOS is added at this stage directly in the mixture to avoid silica demixion during the casting phase and the precipitation of the suspension before its introduction in SBR. The mixtures are then poured into round Teflon molds (diameter = 50 mm, thickness = 10 mm) and let cast in an oven at constant temperature $T_{cure} = 130 ^\circ \text{C}$ under nitrogen flow for 4 h. This yields dry films of about 1 mm thickness.

2.1.2. Internal Mixing Systems. The silica used in systems synthesized by internal mixing is precipitated silica, ZeoSil 1165MP, synthesized and supplied by Solvay. As claimed by the supplier, its specific area is 160 m$^2$/g and its density is 2.06 g/cm$^3$. It is in the form of millimetric pellets, with a multiscale complex structure ranging from the nanometer to more than several microns. Silica–SBR nanocomposites are formulated by stepwise introduction and mixing of SBR chains with silica pellets in a standard internal mixer (Haake).\textsuperscript{3} The mixing chamber is preheated at about 120 °C, in order to obtain the same final mixing temperature of $160 \pm 5 ^\circ \text{C}$, and thus a comparable thermomechanical history. For this reason, the rotor speed is adjusted during the process between 95 and 105 rpm. The polymer is introduced first, in the form of centimetric lamellae, and sheared for 30 s. Then, the powdery mixture of silica pellets, DPG (diphenylguanidine, 1 wt %), and dispersing agent (8 or 16 wt % with respect to silica) is added in two steps. The mixing is then continued until reaching a 1 min long temperature plateau. This run is achieved after typically 5 min. The resulting system is then
removed from the mixing chamber and homogenized by 15 lamination passes in the 1 mm gap between rotating cylinders of a two roll mill. The silica volume fractions reported here were measured by thermogravimetric analysis (TGA).

2.2. SAXS and USAXS Experiments. SAXS measurements were performed on several beamlines. Industrial systems, and pure Zeosil165MP, were measured at ESRF (Grenoble) on the beamline ID02, with a wavelength of 1 Å (E = 12.4 keV) and two sample-to-detector distances of 1 and 10 m, yielding a total Q range from 1 × 10⁻³ to 5 × 10⁻¹ Å⁻¹. On the same beamline, the Bonse-Hart setup allowed to reach the lower Q value of 3 × 10⁻⁴ Å⁻¹. Model systems were measured at SOLEIL (Saclay) on the beamline SWING, with a wavelength of λ = 1.77 Å (E = 7 keV) and two sample-to-detector distances of 1.4 and 6.5m, yielding a total Q-range from 1 × 10⁻³ to 1.5 × 10⁻¹ Å⁻¹, and on the beamline ID02 with the Bonse-Hart setup. Samples were placed in the beam after accurate measurement of their thickness. For each configuration, the 2D-scattering patterns were radially averaged around the direct beam position. The resulting 1D intensity I(Q) data obtained in absolute units were then merged to obtain the final spectrum for one sample. In filled systems, we measure the silica scattering due to the scattering contrast existing between SBR and silica: the scattering length densities of the additives are close to the scattering of the unfilled system, the pure silica scattering in a nanocomposite of the silica volume fraction φSiO₂ = 4.7% v/v (red open circles), 9.1% v/v (blue open circles), and 16.7% v/v (green open circles). The full black line is the best fit result of the primary aggregate form factor calculated with eq 7.

2.3. Transmission Electronic Microscopy (TEM). For TEM characterization, samples were cut by ultracryomicrotomy (mechanical cut) at −80 °C (lower than the glass transition temperature of SBR) at a desired thickness of 50 nm and then laid on a TEM grid. Observations were then realized by a Philips CM200 (200 keV, LaB6) microscope in bright field mode. Pictures were digitized by a CCD (10 Mpixels) for further analysis.

2.4. Oscillatory Shear Experiments. The rheological response in the linear regime of the nanocomposites was obtained with a stress-controlled rheometer MCR-301, used in the strain-controlled mode in plate–plate geometry (20 mm diameter). We cut some disks out of the films for the plate–plate oscillatory shear cell. Isothermal frequency sweeps from 100 to 0.1 Hz were performed at fixed low deformation level (γ = 0.1%), zero normal force, at the temperature of 50 °C.

3. RESULTS AND DISCUSSION

3.1. SAXS/USAXS. SAXS/USAXS is a powerful technique to probe the dispersion of nanoparticles inside a polymer matrix. For X-rays, the scattering length density ρ of silica is very high compared to the one of SBR. This gives high scattering contrast. The scattering length densities of the additives are close to the one of SBR and thus do not contribute significantly to the scattering signal. When mixed with a polymer matrix, the primary nanoparticles can organized in multiscale structures due to van der Waals attraction: they can form primary aggregates that can themselves form secondary larger structures, called usually agglomerates or secondary aggregated level. The understanding of these complex structures as a function of the primary particle concentration is often disturbed by eventual modification of the primary aggregates form factor as well as by the superposition of the structure factor contribution. The form factor of a fractal

Figure 1. SAXS and USAXS scattering of SBR nanocomposites filled with Ludox silica particles in the presence of (a) 1 equiv of the coating agent (O₁), (b) 1 equiv of the coupling agent (Si₁), (c) 2 equiv of the coating agent (O₂), and (d) 2 equiv of the coupling agent (Si₂) at fixed silica volume fraction. The intensities have been normalized by the silica volume fraction configuration, the 2D-scattering patterns were radially averaged around the direct beam after accurate measurement of their thickness. For each sample, the matrix contribution, according to the following operation: IωSiO₂ ≜ Iωsample − (1 − ¼ φSiO₂) × IωMatrix. The intensities have been normalized by the silica volume fraction configuration, the 2D-scattering patterns were radially averaged around the direct beam after accurate measurement of their thickness. For each sample, the matrix contribution, according to the following operation: IωSiO₂ ≜ Iωsample − (1 − ¼ φSiO₂) × IωMatrix.

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aggregate made of a finite size number \((N_{agg})\) of native beads (of radius \(R_0\) and of polydispersity \(\sigma\)) arranged according to a more or less ramified order \((D_i)\) can be described as follows. The scattering function presents three distinct behaviors as a function of \(Q\) separated by two cut-offs \(Q_{C1}\) and \(Q_{C2}\).

(i) At very large \(Q\) (for \(Q > Q_{C2}\)), the scattering can be identified with the form factor of the primary particle, assumed to be a compact sphere:

\[
F(Q) = \left[3f(QR)^2\right]^2 \quad \text{with} \quad f(x) = \frac{\sin(x) - x \cos(x)}{x^3}
\]

where \(R\) is the radius of the sphere. The polydispersity in size is described by a log-normal distribution with the mean radius \(R_0\) and the polydispersity \(\sigma\), where \(\sigma\) is the standard deviation from the mean radius.

\[
P(R, R_0, \sigma) = \frac{1}{\sqrt{2\pi R_0\sigma}} \exp\left(-\frac{1}{2\sigma^2} \left[\ln\frac{R}{R_0}\right]^2\right)
\]

The form factor with polydispersity is calculated by integration:

\[
F(Q) = \int P(R, R_0, \sigma)F(Q, R) \, dR
\]

(ii) At intermediate \(Q\) (for \(Q_{C1} > Q > Q_{C2}\)), the scattering function scales as

\[
F(Q) = Q^{-D_i}
\]

where \(D_i\) is the fractal dimension of the aggregates.

(iii) At low \(Q\) (for \(Q > Q_{C1}\)), the scattering is reduced to

\[
F(Q) = N_{agg}P(Q \to 0, R)
\]

\(N_{agg}\) is the number of primary particle per aggregates. The form factor of the aggregates can finally be expressed as a function of the native beads form factor as follows:

\[
P_{agg}(Q) = N_{agg}Q^{-D_i} \int_0^\infty P(Q, R)L(R, \sigma)R^3 \, dR
\]

The total scattering intensity resulting from a SBR–silica nanocomposite can then be expressed as follows:

\[
I(Q) = \varrho_{SiO_2} \Delta \rho^2 V P_{agg}(Q) S(Q)
\]

where \(\varrho_{SiO_2}\) is the volume fraction of the silica particles, \(\Delta \rho^2\) is the contrast term defined as \((\rho_{SBR} - \rho_{silica})^2\), and \(V\) is the average characteristic volume of the aggregate. \(S(Q)\) represents the full structure factor including all the interactions between the different entities of the system that will depend on the processing conditions.

**3.1.1. Solvent Casting Systems.** The different series of samples containing 1 or 2 equiv (1 or 2 TEOS group per nm² of silica) of coating agent (respectively \(O_1\) and \(O_2\)) or coupling agent (respectively \(Si_1\) and \(Si_2\)) have been analyzed by a combination of SAXS and USAXS measurements for various silica volume fractions. The scattering curves are presented in Figure 1a for \(O_1\), Figure 1b for \(Si_1\), Figure 1c for \(O_2\), and Figure 1d for \(Si_2\). In each case, the curves normalized to the silica volume fraction superimpose nicely in the high \(Q\) region, illustrating a good correction from sample thickness and transmission measurements. In this high \(Q\) domain, the intensity decreases like \(Q^{-4}\) according to the smooth surface of the silica particles with a characteristic oscillation (at \(Q = 7 \times 10^{-2} \text{ Å}^{-1}\)) coming from the form factor of the primary particles. The volume fraction independent slope change visible at \(Q \sim 5 \times 10^{-2} \text{ Å}^{-1}\) can be attributed to interparticle interactions inside the aggregates. At \(Q = 0.01 \text{ Å}^{-1}\), we can see either a maximum or an oscillation which varies with the samples: this characterizes the interaction between the primary aggregates.

At lower \(Q\) values, we can see either a plateau corresponding to aggregates of finite size or a power law behavior indicating that the primary aggregates organize according to a second level of aggregation. For each type of agent, we observed for the two agent concentrations and for all silica fractions a superimposition of all scattering curves in the high and intermediate \(Q\) range: the local organization of the particles, namely the primary aggregates, is the same. Ignoring for the moment the influence of the inter-aggregates spatial correlations, we can fit the data with the most simple physically meaningful formula, the form factor of the primary aggregates calculated using eq 6 and the corresponding full intensity with eq 7. We keep the silica volume fraction \(\varrho_{SiO_2}\) fixed to the experimental value and the contrast term \(\Delta \rho^2\) to the calculated value equal to \(8.01 \times 10^{-2} \text{ cm}^{-1}\). The parameters of the native silica particles \((R_0 = 80 \text{ Å}, \sigma = 0.15)\) have been determined separately with an independent measurement deduced from a diluted suspension of particles and then also fixed.\(^{12}\) We have compared the evolution of the adjustments between keeping constant and varying the aggregates form factor when increasing particle concentration. We find the best data adjustments when keeping constant the primary aggregate parameters \((N_{agg}, D_i)\) for every silica volume fraction values. Contrary to intermediate \(Q\), the low \(Q\) behavior is strongly dependent on the type and concentration of additive as well as on the particle volume fraction: the intensity is decreasing when increasing the silica volume fraction for the \(O_1\) series while it is increasing with the silica concentration for \(Si_1\) and \(O_2\).

The compactness of the primary aggregates can be determined from the aggregation number and the fractal dimension with

\[
\kappa = N_{agg}\left(\frac{R_0}{R_{agg}}\right)^3
\]

where

\[
R_{agg} = N_{agg}^{1/D_i} R_0
\]

We report in Table 1 the parameters deduced from the analysis to illustrate the variations of the morphologies of the primary aggregates as a function of the interfacial additives.

When the curve exhibits a plateau as for the \(O_2\) series at 9.1% \(v/v\) (Figure 1c), the radius of gyration of the primary aggregate

<table>
<thead>
<tr>
<th>Sample</th>
<th>(N_{agg})</th>
<th>(D_i)</th>
<th>(R_{agg}) (Å)</th>
<th>(\kappa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS-O₁</td>
<td>6</td>
<td>1.6</td>
<td>245</td>
<td>0.21</td>
</tr>
<tr>
<td>LS-O₂</td>
<td>6</td>
<td>1.6</td>
<td>245</td>
<td>0.21</td>
</tr>
<tr>
<td>LS-Si₁</td>
<td>2.5</td>
<td>1.4</td>
<td>154</td>
<td>0.35</td>
</tr>
<tr>
<td>LS-Si₂</td>
<td>2.5</td>
<td>1.4</td>
<td>154</td>
<td>0.35</td>
</tr>
</tbody>
</table>

\(^{a}\)Determined from eqs 6 and 7. \(^{b}\)From eq 9. \(^{c}\)From eq 8.
can be determined from the Guinier approximation (\(R_{g,\text{agg}} = 190 \text{ Å}\)). Knowing the radius of gyration of the primary particle \(R_{g,\text{part}} = (3/5)^{0.5} R_0 = 62 \text{ Å}\), we can calculate the compactness with \(\kappa = N_{agg}(R_{g,\text{agg}}/R_{g,\text{part}})^3 = 0.21\), which shows a good agreement between both routes of determinations. We do not observe any significant influence of the amount of the additive on the value of compactness. However, we can see that the aggregates are significantly denser and smaller with the coupling agent (Si69) than with the coating agent (OCTEO). Finding that the morphology of the primary aggregates is independent of the filler content is consistent with the idea that during solvent casting the aggregation is stopped for kinetic reasons by the increase in viscosity with evaporation.\(^{10}\) This is also the possible reason to explain that we can obtain fractal clusters of finite size presenting fractal dimension lower (1.4, 1.6) than the classical values (around 2 for DLA or RLA process).\(^{12}\) This effect seems to be more pronounced for the coupling agent: in this case the slowing down can also be mediated by the covalent bonds formed with the matrix chains.

Knowing the form factor of the aggregates, we can extract the full structure factor \(S(Q)\) using eq 7 by dividing the total intensity \(I(Q)\) by \(P_{agg}(Q)\). The resulting full structure factors \(S(Q)\) are reported in Figure 2a for O1, Figure 2b for O2, Figure 2c for Si1 as a function of the particle concentration, and Figure 2d for a comparison between Si1 and Si2 at fixed silica concentration.

The full structure factor \(S(Q)\) can be decomposed to

\[ S(Q) = S_{\text{inter agg}} \times S_{\text{intra agg}} \times S_{\text{secondary agg}} \]  

where \(S_{\text{inter agg}}\) represents the interactions between the primary aggregates, \(S_{\text{intra agg}}\) the interactions between the native particles inside the primary aggregates, and \(S_{\text{secondary agg}}\) represents the secondary aggregation organization of the primary aggregates at larger length scale. We can see clearly in Figure 2 the three contribution of the full structure factor: at large \(Q\), the correlation between the native beads inside the primary aggregate \(S_{\text{intra agg}}\) induces a correlation hole; in the intermediate \(Q\) range, a nice repulsion peak illustrates the inter aggregates interactions \(S_{\text{inter agg}}\), and at lower \(Q\) the contribution of the secondary structure that follows a power low behavior.

Figure 2. Full structure factor \(S(Q)\) calculated from eq 7 as a function of the particles concentration (red 4.7, blue 9.1, and green 16.7% v/v) for a (O1), b (Si1), c (O2), and d (Si2). In the inset, the full color lines illustrate the modeling of the interaggregate interactions using the PY function eq 12.
The structure factor is given by

$$S(Q) = \frac{1}{1 - \bar{N}(Q)}$$

(12)

We have tried to add an additional PY function to model the interactions between the native particles inside the primary aggregates by setting the interparticle distances to particles in close contact (2R0). However, the calculation gives systematically a smaller interparticle distance. That can be due to the morphology of the primary aggregates presenting low aggregation numbers (~10) and reduced compactness (Df < 2). This decreases the number of nearest neighbors in contact at every location in the aggregates. It is known that in this case the repulsion peak is limited to an oscillation which is not reproducible by a PY function. In addition, polydispersity effects can enhance the disagreement between the PY function (monodisperse) and the scattering curve. Another origin of this disagreement could be due to the fact that particles interact simultaneously via a short-range attractive potential, modeled with the Lennard-Jones potential, and a long-range repulsive Yukawa potential. This idea of a "hybrid" repulsive/attractive potential has been probe by numerical simulation by Mossa et al.38 that show various cluster morphologies depending of the repulsive/attractive balance. The depth of the correlation hole can be related to the strength of attraction that appears to be dominant here, which may be due to the presence of residual water induced by particle solvent transfer. However, such a hybrid potential must be difficult to implement using only simple analytical considerations.

The signature of the secondary structure formed by the primary aggregates behaves mostly like a power law without finite size cut-off in the probed Q range as illustrated in Figures 2a,b,d. This means that this secondary structure can be due either to very large fractal objects or to fractal network. We can observe that the secondary structure is strongly dependent on the nature, the quantity of interfacial additives, and the filler volume fraction. The slope of the power law and the low Q cut-off are decreasing when the particle concentration increases for the series O1 (Figure 2a), meaning a reduction of the compactness of the secondary structure. A reverse situation is observed for the O3 series (Figure 2c) which exhibits a nice plateau when the particle concentration increases. This plateau is the signature of finite size objects formed as a result of the organization of the primary aggregates. The size of such finite size objects can be determined using the classical Guinier approximation which gives here Ragg = 580 Å corresponding to a spherical objects of Ragg = R0 (S/3)1/2 = 749 Å. This size can also be determined from the aggregation number, that is, the number of primary aggregates constituting the agglomerates which is directly given here by the extrapolation of S(Q→0) ~ S4, the fractal dimension of the agglomerates given by the slope ~1.5, and the size of the primary aggregates Ragg = 245 Å. We obtain Ragg = Ragg (S) primary agg = 754 Å.36

Most important now is the possibility to describe quantitatively the interaggregate spatial correlations and their evolution as a function of the nature, the quantity of additive, and the filler content. This can be modeled correctly with the PY function, as nicely showed in the inset of Figure 2 for the O3 series. The same could be shown for the Si1 series. We can extract the interaggregate distance dinter as well as the effective volume fraction of the interacting objects. We wish to distinguish two cases. When the primary aggregates do not form a secondary structure, the effective volume fraction deduced from the PY calculation is equal to the effective volume fraction of primary aggregates. This effective volume fraction can be estimated according to

$$\varphi_{agg} = \left(\varphi_{SiO}/N_{agg}\right)\left(1/D_{agg}\right)^3 = \frac{\varphi_{SiO}}{\kappa}$$

(13)

A good example of such absence of secondary structure is the case of Si1 at 4.7%. We obtain \(\varphi_{eff\,inter} = 0.13\) with the PY fit while we can deduced from the modeling of the form factor of the primary aggregate a compactness value \(\kappa = 0.35\), giving \(\varphi_{agg} = 0.047/0.35 = 0.135\). When the primary aggregates form a secondary structure, such equality between \(\varphi_{eff\,inter}\) and \(\varphi_{agg}\) is no more respected because the effective potential between the primary aggregates is modified by the secondary structure. However, we can follow the variations of the interaggregate interactions with different experimental conditions. This is illustrated in Figure 3 by the variation of the dinter parameter as a function of the silica volume fraction for the different casting systems. We can observe that the interacting distances tend to increase (or stay constant for O1) with the coating agent while they tend to significantly decrease for the coupling agent (Si1). This suggests that the coupling agent induces more attractive interactions between the primary clusters while the coating agent seems to generate more repulsive interactions. Remembering the sizes of the clusters (245 Å for coating and 154 Å for coupling agent), this induces the interpenetration between the clusters, possibly more pronounced with the coupling agent.

3.1.2. Internal Mixing Systems. We turn now to the samples prepared by internal mixing and using precipitated silica Zeosil 1165MP filler. The variation of the scattering signal is rather monotonic with the filler concentration and does not present obvious differences with the interfacial additives as illustrated by
Figure 3. Variation of the primary cluster interacting distance $d_{0 \text{ intra}}$ as a function of the silica volume fraction for the different solvent casting systems LS-O₁ (black), LS-O₂ (blue), and LS-Si₁ (red).

<table>
<thead>
<tr>
<th>sample</th>
<th>4.7% v/v</th>
<th>9.1% v/v</th>
<th>16.7% v/v</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS-O₁</td>
<td>650</td>
<td>550</td>
<td>550</td>
</tr>
<tr>
<td>LS-Si₁</td>
<td>480</td>
<td>420</td>
<td>300</td>
</tr>
<tr>
<td>LS-O₂</td>
<td>650</td>
<td>650</td>
<td>850</td>
</tr>
<tr>
<td>LS-Si₂</td>
<td>450</td>
<td></td>
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</table>

Table 2. Interaggregates Distance $d_{0 \text{ inter}}$ Deduced from the Scattering Curves Analysis Using Eq 12 for the Systems Prepared by Solvent Casting (We Estimate the Range of Uncertainties Equal to ±15%)

The main difference with the model solvent casting systems is that the form factor of the primary aggregates is varying when the silica volume fraction is increasing: both the aggregation number and the fractal dimension are decreasing with increasing silica volume fraction, leading to a decrease of the mean aggregate radius (Figure 5a) with a constant compactness (Figure 5b). This result is not surprising regarding the sample processing used here for which the mechanical constraints inside the internal mixer are correlated with the filler content: larger particles loading increases the shearing forces, which can break more the agglomerates and therefore reduce the primary aggregation. The primary aggregates are also larger and denser than the solvent casting clusters.

The silane agents have a major impact on the constitutive variables: the primary aggregates are smaller ($\bar{R}_{\text{agg}}(\text{Si}) < \bar{R}_{\text{agg}}(\text{O})$) and denser ($\bar{k}(\text{Si}) > \bar{k}(\text{O})$) with the coupling agent than with the coating one, and this result is consistent with the ones obtained with solvent casting systems. That suggests that the covalent bonds between the coupling agent and the chains of the matrix act as a limitation of the aggregation process either in solvent casting or in internal mixing. In Figure 5c, we observe that the interacting distance is systematically decreasing with the filler content for all the systems. We can also observe that the distances are smaller for the coupling than for the coating agent. That suggests that the interactions between the clusters are managed by the interfacial agents: shorter distances suggest more effective attractions as a result of the effect of the coupling agent while larger distances suggest more repulsive interactions obtained with the coating agent. This observation is again consistent with the one made for the solvent casting systems. In the case of overlap between the clusters, one can thus expected a more important degree of interpretation with the coupling than with the coating agent.

We do not try to go further in the analysis of the low Q scattering contribution, which here appears to be comparable in the different systems. We believe this is due to a small amount of
large agglomerates. In principle, we should find a self-consistency between the number of particles effectively introduced in the sample ($\phi_{SiO_2}$) and the number of particles that are interacting ($\phi_{inter}$, $\phi_{intra}$). This is however not obvious because the number of particles involved in the secondary low $Q$ aggregation process remains difficult to estimate with the informations available in the SAXS spectrum at low $Q$.

3.2. Transmission Electronic Microscopy. To complete the structural determination by SAXS and probe the homogeneity of the dispersion at larger scale, we have performed TEM experiments on various systems. An example is given in Figure 6 for the LS-O2 sample at two particle concentrations: $\phi_{SiO_2} = 4.7\%$ and $16.7\%$ using two magnifications. For the diluted sample, we can see the primary particle are forming finite size aggregates whose size, aggregation number, and fractal dimension are in good agreement with the "picture" of the primary aggregates extracted from the SAXS determination. The typical distance between the primary aggregates for both diluted and concentrated case are also in agreement with the ones deduced from the PY analysis (see Table 2). When increasing the particle concentration, the number of primary aggregates increases, and we can see the formation of a primary connected network in Figure 6c,d. In the limited range of observed images, we do not see any larger objects even at low magnification. That suggests that the low $Q$ intensity visible on the SAXS curves should be related to a secondary network as a result of the arrangement of the primary aggregates. This is supported by the variation of the low $Q$
intensities that depend not only on the filler concentration but also on the nature and the quantity of surface agent. However, a quantitative description of this secondary arrangement remains difficult to perform even in the real space.

An example of samples prepared by internal mixing is also presented in Figure 7 for the case of the M-Si1 at two concentrations, 8.4% (top) and 15.3% v/v (bottom), and two different resolutions. The primary aggregates appear indeed here larger and more compact than for the casting systems as a confirmation of the results obtained from the SAXS analysis. When increasing the filler concentration, the homogeneity of the filler dispersion is decreasing. We also observe some large and compact black spots. The low Q SAXS intensity is related to the presence of these few large objects, whose typical size is decreasing when the filler content is increasing, followed by the decrease of the low Q intensity seen in Figure 3. Despite some remaining questions about the secondary structure of the aggregates, we show a good qualitative accordance between the TEM and SAXS analysis about the form factor of the primary aggregates and the formation of the primary network.

3.3. Viscoelastic Behavior. The rheological behavior of the materials has been investigated using a low shear apparatus at a temperature of reference T = 50 °C that enables to cover a frequency range from 628 to 0.0628 rad/s (100 to 0.01 Hz). We compare the behavior of the pure SBR matrix with one of the filled samples when increasing the silica volume fraction for the different additive quantity (1 or 2 equiv of coating agent or of coupling agent). Figure 8 presents the variation of G’ and G” as a function of the frequency (rad/s) for the Ludox systems (Figure 8a for LS-O1 and Figure 8b for LS-Si1) and for the Zeosil1165MP systems (Figure 8c for M-O1 and Figure 8d for M-Si1). The series with 2 equiv of additive are not reported but present a similar evolution. For pure SBR matrix, the curve has the usual shape in log−log representation. At a lower pulsation, a decrease with G’(ω) ∼ ω² can be, as usual, associated with the liquid state of the polymer. At intermediate pulsation, between 100 and 1 rad/s, the height of the plateau (taken at 100 rad/s) allows to estimate the entanglement mass of the polymer.

\[ G_N \sim 5.85 \times 10^5 \text{ Pa} \] is found for the matrix prepared by internal mixing which allows to determine \( M_e = 2.5 \text{ kg/mol} \), in agreement with reported values. We found a lower value, \( G_N \sim 4.31 \times 10^5 \text{ Pa} \), for the matrix prepared by solvent casting which therefore seems to abate the degree of entanglement. The influence of the solvent casting on the molecular mass distribution has been checked by gas chromatography and does not reveal any significant modification of the molecular mass of the chain. Measuring the frequency at the intersections between G’ and G”, one can...
determine the reptation time that is equal to 14 s for the matrix prepared by internal mixing, in agreement with the molecular mass used of 140 kg/mol. We find a shorter time for the matrix prepared by solvent casting, equal to 5 s, which agrees with the idea of a decrease of the entanglement density induced by the solvent casting preparation.

The behavior of the silica-filled samples is roughly similar whatever the additive and the sample processing condition. At high frequency, we can observe a continuous increase of the modulus level without a significant change of the curve shapes. This progressive increase of $G'$ with silica fraction is analogous to elastic reinforcement as expected. Conversely, at low frequency, a much more differentiated behavior is observed: adding silica greatly increases the terminal times.

We focus mainly on the reinforcement properties of the materials by determining the reinforcement factor given by the elastic modulus ratio between the filled sample and the pure matrix on the rubbery plateau typically at 100 rad/s and its variations with the filler content and with the interfacial additives. The evolution of the reinforcement factor with the particle concentration can be quantitatively described with a theoretical model proposed by Takayanagi\textsuperscript{40} and already described in detail in ref 15. We choose an approach, called the mechanical percolation model, which consists in a series-parallel model extended with a percolation concept. In this model, the composite is described by a parallel mechanical coupling of a rigid phase (primary network), made of a theoretical volume fraction of filler network, and a soft one, made of the matrix reinforced with the fillers out of the network (i.e., isolated aggregates or agglomerates and or secondary network). This two-phase model is consistent with the multiscale structure of our samples, where the primary network is in line with the percolation of the primary clusters and the secondary structure can play the role of the fillers for the soft phase. The network volume fraction is calculated from the percolation theory. In the case of randomly distributed objects, the volume fraction $\Phi$ of

<table>
<thead>
<tr>
<th>sample</th>
<th>filler content (%)</th>
<th>$\varphi_{\text{intra}}$</th>
<th>$\varphi_{\text{inter}}$</th>
<th>$d_{\text{inter}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-O$_2$</td>
<td>8.4 0.025 0.030 1300</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>12.0 0.024 0.030 1200</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>15.3 0.030 0.030 1000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>18.4 0.035 0.040 900</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>21.0 0.040 0.050 800</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-Si$_1$</td>
<td>8.4 0.030 0.080 950</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.0 0.032 0.110 800</td>
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<td></td>
<td>15.3 0.035 0.130 700</td>
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<td></td>
<td>18.4 0.035 0.130 600</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>21.0 0.040 0.130 550</td>
<td></td>
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<tr>
<td>M-O$_2$</td>
<td>7.9 0.035</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>11.1 0.033</td>
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<td></td>
<td></td>
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<tr>
<td></td>
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<td>16.7 0.035 0.050 1000</td>
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<td>M-Si$_2$</td>
<td>7.9 0.030 0.060 1100</td>
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<td>11.3 0.033 0.080 750</td>
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<td></td>
<td>14.1 0.035 0.100 700</td>
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<td></td>
<td>16.2 0.020 0.110 550</td>
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<td></td>
<td>19.2 0.020 0.110 500</td>
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Figure 6. TEM images for the sample LS-O$_2$ at low filler concentration 4.7% v/v at low magnification scale bar = 500 nm (a) and high magnification scale bar = 100 nm (b) and large filler concentration 16.7% v/v at low magnification scale bar = 500 nm (c) and high magnification scale bar = 100 nm (d).

Figure 7. TEM images of SBR matrix prepared by internal mixing at low filler concentration 8.4% v/v of silica particles (160MP) (top) and two magnifications (a) scale = 1 μm and (b) scale = 100 nm. Bottom: SBR matrix prepared by internal mixing at large filler concentration 15.3% v/v of silica particles (160MP) and two magnifications (a) scale = 1 μm and (b) scale = 100 nm.
percolated structure depends on the total volume fraction of objects, $\phi_{\text{eff}}$, and is given by

$$\Phi(\phi_{\text{eff}}) = 0 \quad \text{for} \quad \phi_{\text{eff}} < \phi_c$$

$$\Phi(\phi_{\text{eff}}) = \left(\frac{\phi_{\text{eff}} - \phi_c}{1 - \phi_c}\right)^\beta \quad \text{for} \quad \phi_{\text{eff}} > \phi_c$$

(14)

with $\phi_c$ the percolation threshold and $\beta$ the critical exponent. As assumed by De Gennes, the dead branches do not participate actively in stress transmission, and taking account only of the structure backbone requires a value of $\beta$ close to 1.8. The shear modulus, $G$, of the composite is then given by

$$G = \frac{1 - 2\nu(\phi_{\text{eff}}) + \Phi(\phi_{\text{eff}}/\phi_c)G_{\text{network}} + (1 - \phi_{\text{eff}})\Phi(\phi_{\text{eff}})G_{\text{matrix}}^2}{(1 - \phi_{\text{eff}})G_{\text{matrix}} + (\phi_{\text{eff}} - \Phi(\phi_{\text{eff}}))G_{\text{network}}}$$

(15)

$G_{\text{matrix}}$ is the modulus of the pure matrix, and $G_{\text{network}}$ is the one of the filler percolating network. The calculation has been done using the primary aggregates compactness $\kappa$ deduced from the scattering curves to estimate $\phi_{\text{eff}}$ as a function of the particle filler volume fraction $\phi_{\text{SiO}_2}$, according to eq 13. The structural percolation thresholds could be difficult to be determined accurately. For the solvent casting systems, we can use the scattering curves to get reasonable values. The silica volume fraction threshold is chosen on two features: the absence of large scale structure for which the scattering exhibited a plateau and the appearance of the large scale structure for which the scattering curve present an upturn at low Q. This is illustrated in Figure 8.

**Figure 8.** Evolution of the elastic (circles) and loss (lines) modulus as a function of the frequency for the pure SBR matrix (black) and for the nanocomposites prepared by solvent casting filled with increasing silica volume fraction $\phi_{\text{SiO}_2} = 4.7$ vol % (red), 9.1 vol % (blue), and 16.7 vol % (green) containing (a) 1 equiv of the coating agent O, and (b) 1 equiv of the coupling agent Si. Variation of the modulus $G'$ and $G''$ as a function of the frequency for nanocomposites prepared by internal mixing for silica volume fraction equal to 0% (pure matrix), 8.4% (red), 12% (blue), 15.3% (green), 18.4% (orange), and 21% (gray) for (c) 1 equiv of coating agent and (d) 1 equiv of coupling agent.

**Table 5. Parameters Resulting from the Analysis Using the Percolation Model Described with Eq 15 (Full Black Line) on Figure 9 Obtained for All the Systems (Casting and Mixing)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>OCTEO</th>
<th>Si69</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LS-O1</td>
<td>LS-Si1</td>
</tr>
<tr>
<td>$\phi_{\text{SiO}_2},\text{structural}$</td>
<td>0.05</td>
<td>0.07</td>
</tr>
<tr>
<td>$G_{\text{network}} \pm 20%$ (Pa)</td>
<td>$3.75 \times 10^6$</td>
<td>$6.50 \times 10^6$</td>
</tr>
<tr>
<td>$\phi_{\text{SiO}_2},\text{mechanical}$</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>$\kappa_{\text{agg}}$, mechanical*</td>
<td>0.19</td>
<td>0.09</td>
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</table>

*Calculated with eq 13.
Figure 1. For LS-O₁ (Figure 1a), the lower silica volume fraction already exhibited a low Q upturn, and thus the percolation threshold is fixed at 5% as reported in Table 5 (φ_{SiO₂ structural}). For LS-Si₁ (Figure 1b), the upturn appears between 4.7 and 9.1% and thus leads to fix the threshold at 7%. For the systems prepared by internal mixing, we have used TEM pictures reported in Figure 7 to determine the thresholds which can be fixed at 10% for every systems. These values are consistent with the one reported recently on similar systems and supported by TEM and rheology.

The reinforcement factor determination is not precise and presents large error bars (estimated here reasonably around ±20%). However, we succeed in reproducing correctly all the experimental data for all sample preparation modes, filler content, nature, and quantity of interfacial additives. This gives us a general picture of the viscoelastic behavior of our nanocomposites and the correlations with the filler network structure as a function of the different parameters.

We first observe that below the percolation the reinforcement is mostly driven by the compactness of the primary aggregates, this being independent of the size of the objects. As seen in Figure 5a, for a given agent, the mean radius of the aggregates can be larger by a factor 2−3 for the internal mixing preparation while leading to comparable cluster compactness (Figure 5b) with resulting very close reinforcement values.

The second point is that we observe a systematic shift of the structural percolation threshold toward smaller critical percolation filler volume fraction values, typically by a factor 2−3 per case. This result is independent of the systems and thus on the initial criteria used to determine the structural percolation threshold. That is suggests that a mechanical percolation threshold could arise faster than the structural one. Knowing the cluster compactness from SAXS, we can calculate the corresponding critical primary aggregate volume fraction (Table ...
5). We found a nice consistency of the obtained values with the nature of the agent, with a critical primary aggregate volume fraction around 10% for the coupling agent and 25% for the coating agent, independent of the preparation mode and in agreement with the range of cluster morphologies: with Si69, the percolation threshold is lower for lower sized and denser clusters, as usually observed in nanocomposites.

We can determine an effective filler network density using simple geometrical considerations: assuming the primary clusters of size \(d_{agg}\) are organized inside a cubic network of typical size \(d_0\) inter, the filler network density can be expressed as 

\[
\rho_{network} = \left(\frac{\pi}{6}\right)\left(\frac{d_{agg}}{d_0\text{ inter}}\right)^3.
\]

This traduces the degree of interpenetration between the primary clusters after the percolation threshold and can be calculated for all the systems for a common value of silica volume fraction equal to 16 vol %. The network modulus deduced from the percolation model is found to vary as a function of the power three of the filler network density according to the rubber elasticity prediction. The filler interpenetration acts as the variation of the cross-linked junctions of the network.\(^{42}\) This is highlighted on Figure 10, which shows the linear trend of \(G^{1/3}\) as a function of \(\rho_{network}\). The lower value of the filler network density (around 10%) is consistent with the silica volume fraction (16 vol %). The extrapolation of the modulus toward low density gives rise to a modulus corresponding to reinforcement factor of 4−5, which is consistent with usual values found with silica at the percolation point.\(^{5,10,13,26}\) Such a representation permits to summarize the observations described previously about the sizes and the distances between the clusters inside the network (Figures 3 and 5). We can thus observe that the network density is driven by the interfacial agent type, the quantity of additive, and the sample preparation: 2 equiv of coupling agent lead to a denser network through attractive interactions when 2 equiv of coating reduced the density by the way of repulsions. This is in line with the filler−matrix bonding effect available with the coupling agent. At the same time, the degree of interpenetration is more pronounced for samples prepared by internal mixing than for the samples prepared by solvent casting. That could be the result of the shearing effect submitted by the clusters during the mixing process.

We do not consider any “bound layer” here usually observed in similar systems as a 1−2 nm thickness layer of polymer around the filler that would contribute to the mechanical behavior of the materials. We think that such bound layer could affect the absolute values of the rigid phase modulus but not their relative variations with the filler network structure. A specific study is necessary to evaluate the silane agent effect on the quantity and extension of the bound layer. We can also observe that the different secondary structures of the network highlighted with scattering/TEM, either large or compact agglomerates for internal mixing systems or secondary network for solvent casting system, do not seem to have an influence on the reinforcement. That suggests that only a few very large agglomerates, dead branches, or network with a very large scale mesh size do not participate to the viscoelastic behavior at the given (high) frequency. The anomalous flow behavior, not studied in the present paper, is still an open question in nanocomposites as it remains a complex problem involving both filler network and polymer chains conformation and dynamics.\(^{43}\) This will be the scope of a future publication.

4. SUMMARY AND CONCLUSION

We have analyzed the filler network structure and the reinforcement properties of a series of SBR/silica nanocomposites prepared either by solvent casting with well-defined colloidal silica particles or by internal mixing with precipitated silica (Zeosil 1165MP) using either a coating interfacial agent OCTEO (O) or a coupling interfacial agent Si69 (Si) for various filler volume fractions. Using an analytical function to fit the SAXS scattering, we have been able to quantitatively describe the multiscale organization of the particles inside the matrix, by separating the contribution of the cluster form factor from the contribution of the spatial correlations between the clusters. The multiscale structure of the filler has been confirmed by TEM experiments on the samples. For all sample processing conditions, the interfacial coupling agent leads to the formation of smaller and denser primary aggregates that are forming a narrowing network due to cluster−cluster overlap. Conversely, the coating agent produces larger and ramified aggregates leading to a more opened network. The mechanical analysis using a percolation model shows that the viscoelastic properties on the rubbery plateau are controlled by the primary network where the secondary large scales structures have a limited influence at the investigated frequency. The reinforcement is mostly driven by the cluster compactness below the percolation threshold. We found a shift between the structural percolation and the mechanical percolation threshold that arises faster with coupling agent than with coating agent according to the cluster morphologies. Above the percolation threshold, we demonstrate a quantitative correlation between the reinforced network modulus variation and the filler network density, namely the degree of overlap of primary aggregates inside the network whose strength is mostly driven by the interfacial additive and the sample preparation: the coupling agent as well as the internal mixing tighten the network in a more efficient way with a resulting increase of the modulus. Such an approach is useful to go further into the structure−properties description of such materials like the anomalous flow behavior as well as the chain conformation and the chains dynamics contribution to the viscoelastic properties that will be the scope of future publications.

Figure 10. Variation of the network modulus \(G^{1/3}\) as a function of the filler network density \(\rho_{network} = \left(\frac{\pi}{6}\right)\left(\frac{d_{agg}}{d_0\text{ inter}}\right)^3\) determined for a given silica volume fraction: 16.7% for LS-O1, LS-O2, and LS-Si1, 15.3% for M-O1 and M-Si1, 16.7% for M-O2, and 16.2% for M-Si2.
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Notes
The authors declare no competing financial interest.

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