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Citation: *The Journal of Chemical Physics* **133**, 094902 (2010); doi: 10.1063/1.3469827

View online: <https://doi.org/10.1063/1.3469827>

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Correlation of mass fractal dimension and cluster size of silica in styrene butadiene rubber composites

Gerald Johannes Schneider,^{1,a)} V. Vollnhals,² K. Brandt,³ S. V. Roth,⁴ and D. Göritz²

¹*Institut für Festkörperforschung, Neutronscattering and Jülich Centre for Neutron Science, Forschungszentrum Jülich, 52425 Jülich, Germany*

²*Institut für Physik, Universität Regensburg, 93040 Regensburg, Germany*

³*Deutsches Institut für Kautschuktechnologie e. V., Eupener Str. 33, 30519 Hannover, Germany*

⁴*HASYLAB at DESY, Notkestr. 85, 22603 Hamburg, Germany*

(Received 16 August 2009; accepted 25 June 2010; published online 3 September 2010)

The morphology of the precipitated silica VN3 filled in styrene butadiene rubber was studied as a function of the volume fraction Φ by means of small-angle X-ray scattering experiments. The wide q -range of $0.008 \text{ nm}^{-1} < q < 1 \text{ nm}^{-1}$ probes the structures of the primary particles, the clusters, and resolves a part of the larger clusters of the silica. The diameter of the primary particles and their surface roughness are independent from the silica concentration. The size of the clusters and the corresponding aggregation number depend on Φ . This observation could be ascribed to external mechanical forces because of the mixing process and to growing cluster-cluster interactions with increasing filler fraction. In contrast the mass fractal dimension does not depend on Φ , and by that means experimentally proving that there is not necessarily a correlation between the mass fractal dimension and the cluster size. © 2010 American Institute of Physics. [doi:10.1063/1.3469827]

I. INTRODUCTION

Adding filler particles to polymers significantly modifies the properties of the resulting mixtures in comparison to the pure materials. For example, the permeability and selectivity of polymer membranes can be changed using nanoparticles.^{1–4} If silica and carbon black are used as filler particles a significantly higher modulus of the composite can be achieved.^{5–9}

To study nanoparticles small-angle scattering experiments are very suitable.^{10–12} Schaefer *et al.*¹¹ combined various scattering techniques and impressively proofed the applicability of the concept of a hierarchical structure for silica dissolved in a simple solvent ranging from few angstroms to several tenth of micrometers. However, although a lot of scattering experiments have been performed in order to connect the microstructure with macroscopic properties, e.g., the structure of the silica on the nanoscale and the viscosity of the composite,^{13–15} the situation remains puzzling.

In the present work we study the microscopic structure of the precipitated silica VN3 in a q -range of $0.008 \text{ nm}^{-1} < q < 1 \text{ nm}^{-1}$ by means of small angle X-ray scattering experiments. In particular, information on the primary particles and the clusters of the silica is obtained. In order to separate a possible influence of the external mixer and internal forces arising due to filler-filler and filler-polymer interactions the mixing time was kept constant. The main results are the following. (i) The size of the primary particles as well as their surface roughness are independent from the silica fraction Φ . (ii) The cluster size changes with Φ . It is demonstrated that at higher Φ the cluster-cluster distance is small enough to mutually decrease their size. However, at smallest Φ solely

the mixing process is responsible for decreasing the size of the clusters. (iii) It is shown that the mass fractal dimension is not changed. By that means the experiments demonstrate that there is not necessarily a correlation between the mass fractal dimension and the cluster size. In particular it shows that the cluster size is a finite size effect of the physical object limiting the power law domain of the mathematical fractal.

These results are obtained directly from the scattering diagram without assuming a particular model and can therefore considered to be generally valid. In order to contribute to a deeper insight in the morphology of hierarchical structures and additionally provide basic input for constitutive models of the macroscopic mechanical properties accurate values are decisive. However, this part is very challenging, because of the complex morphology, the scattering diagrams are very complicated.¹¹ In the simplest model the different levels can be ascribed to different fractal dimensions and the positions of the crossovers q_c between two regions can be used to determine the object size d using $d \propto 1/q_c$.¹⁶ On the other hand, sophisticated models exist, which are especially derived to account for such structures. In particular, the unified model of Beaucage¹⁷ is well known and has been successfully applied since several years. Of course, in the ideal case both the simple determination and the model function approach should provide the same results. However, in the case of hierarchical structured silica a systematic comparison has not been performed up to now. Besides the structural characterization of the silica in the composite, we therefore address the very important question of how does the extraction method influence the result. This is of particular importance if the results of different sources should be compiled and compared in order to correlate the microstructure with the macroscopic material properties.

^{a)}Electronic mail: g.j.schneider@fz-juelich.de.

II. EXPERIMENTAL

Styrene butadiene rubber (Lanxess, Leverkusen, Germany) filled with precipitated silica VN3 (Evonik Degussa GmbH, Köln, Germany) and the pure silica powder were studied by means of small-angle X-ray scattering experiments.

A. Samples and sample preparation

The volume fraction Φ of the silica in rubber varies from 2 to 19 vol %. VN3 has a cetyltrimethylammonium bromide (CTAB) surface area of 165 m²/g and a Brunauer, Emmett and Teller (BET) surface area of 170 m²/g.¹⁸ Concerning the primary particle diameter, experiments with the transmission electron microscope (TEM) yield slightly different results of (4–20) nm,¹⁹ (15–20) nm,²⁰ or an average size of 17 nm.²¹ Additionally the samples contain stearic acid (2 phr), sulfur (1.5 phr), and vulcacit (0.13–1.25 phr) depending on the filler fraction. To prepare the unfilled samples, the rubber was plasticized for 1 min. Then the stearic acid was added and the mixture was homogenized for 2 min. In the case of the composites the silica was added together with the stearic acid and the mixing time extended up to 4 min. The vulcanization system was incorporated into the mixtures on a two-roll-mill at 60 °C and a rotor speed of 16 rpm (first roll) and 20 rpm (second roll).

B. Small-angle X-ray scattering experiments

The small-angle X-ray scattering experiments were performed at the beam line BW4 of the DORIS III storage ring at the Hamburger Synchrotronstrahlungslabor (HASYLAB) at the Deutsches Elektronen-Synchrotron (DESY), Hamburg (Germany). The measurements using the standard transmission configuration²² were carried out at a fixed energy of 8979 eV, corresponding to a wavelength $\lambda=0.138$ nm. The scattered intensity was recorded using the two dimensional Mar CCD-detector. The intensity curves $I(q)$ were obtained by radially averaging over a 20° wide segment of a circle and an appropriate subtraction of the background. Absolute calibration was not possible at the time the measurements were performed. To enlarge the accessible range of momentum transfer q and thus the accessible length scale, different sample-detector distances (2 and 12 m) were used.

III. THEORY

The silica studied by the present work consists of primary particles which form clusters due to the high volume concentrations of the samples involved. These clusters are the basic units for larger clusters. By that means a hierarchical structure, consisting of several characteristic length scales, is created. Such an object can be reasonably well described by the concept of fractals. Therefore, most conveniently the scattering diagrams of silica can be analyzed²³ and the measured intensity I can be decomposed in the scattering of the primary particles, the clusters, and larger clusters. In a reasonable approach the primary particles can be represented by spheres with a rough surface, represented by the so-called surface fractal dimension d_s .²⁴ For example, if

the surface is smooth $d_s=2.0$, and if $d_s=3.0$ the surface is infinitely rough.²³ The scattered intensity of a fractal surface is simply²³

$$I \propto q^{-(6-d_s)}. \quad (1)$$

Similarly, the clusters which consist of the primary particles can be described by means of a mass fractal dimension d_f , which represents the branching. For example, if the object is linear then $d_f=1$. When a homogeneous sphere is considered then $d_f=3$. Similar to Eq. (1),²³

$$I \propto q^{-d_f}. \quad (2)$$

Therefore, by means of a double-logarithmic plot of the intensity the slope provides a simple access to the surface roughness or to the mass fractal dimension. Fortunately, the slopes usually observed are different, and therefore the mass and surface fractal ranges can be distinguished very easily.

Frequently the particles involved are polydisperse. Therefore, characteristic oscillations, representing the diameter, which would be observed in the scattering diagrams of spheres if only a single diameter is present, are smeared out. In such a case the positions of the crossovers q_c between the fractal ranges provide the perimeter diameters of the objects d by $d=2\pi/q_c$.²⁵

The unified model of Beaucage has proven to be a very appropriate tool to characterize the multilevel structure of silica. For an arbitrary number N of structural levels it can be written as¹⁷

$$I = \sum_{i=1}^N [G_i \exp(-q^2 R_{g_i}^2/3) + B_i \exp(-q^2 R_{g_{i-1}}^2/3) \tilde{q}^{p_i}] \quad (3)$$

with $\tilde{q}=(\text{erf}(qR_{g_i}/6^{(1/2)}))^3/q$. $i=1$ refers to the smallest structural level, i.e., $R_{g_1}:=r_g$ and $R_{g_2}:=R_g$ are the radius of gyration of the primary particles and the clusters, respectively. p_i refers to the slopes with $p_1=(6-d_s)$ and $d_f=p_2$. Within the experimental window objects smaller as the primary particles are not resolved. Therefore, the high- q exponential cutoff $\exp(-q^2 R_{g_0}^2/3)$ is not needed and hence R_{g_0} is set to zero. Since Eq. (3) contains the local scattering laws, Eqs. (1) and (2), it does not introduce further parameters.

In the case of homogeneous spheres the radius r can be calculated using $r^2=5/3r_g^2$. The perimeter radius R of a spherically isotropic fractal is given by²⁶

$$R^2 = \left(\frac{d_f + 2}{d_f} \right) R_g^2. \quad (4)$$

If the size of the fractal is explicitly drawn into account, then a slightly different relation is obtained,²⁶

$$R^2 = \frac{((d_f + 2)(d_f + 5))}{2d_f(d_f + 1)} R_g^2. \quad (5)$$

In the case of $d_f=3$ Eqs. (4) and (5) equal the relation for a simple sphere.

IV. RESULTS AND DISCUSSION

Figure 1(a) displays the scattering diagrams, i.e., the scattered intensity I as a function of the momentum transfer

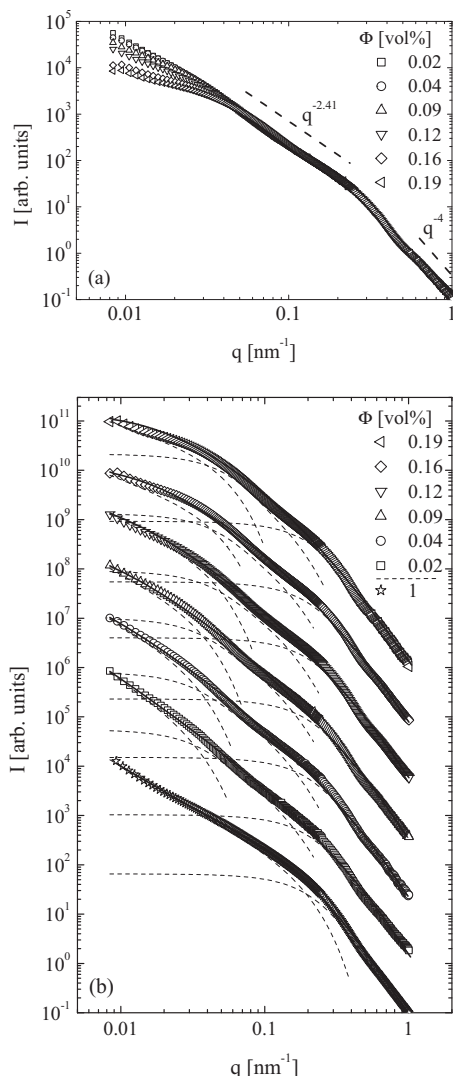


FIG. 1. Scattered intensity of silica in rubber as a function of the momentum transfer q . The silica fraction varies from 2 to 19 vol %. (a) Normalized data. (b) Scaled scattering diagrams including the pure silica curve. The lines represent the fit, cf. text.

q , of silica filled styrene butadiene rubber. The filler fraction varies from 2 to 19 vol %. The intensity curves are normalized to $I(q=1 \text{ nm}^{-1})=1$ to better visualize both differences and similarities. The symbols represent the experimental data. Error bars are smaller than the symbol size and therefore omitted for the sake of clarity. Except the intensity at the small q -values the scattering diagrams are identical with a slope of -4 at large q and a slope of -2.41 in the intermediate region, visualized by the dotted lines.

In order to extract constitutive parameters, the diagrams were fitted by the unified model of Beaucage [Eq. (3)] represented by the full lines in Fig. 1(b). For the sake of clarity the displayed curves are multiplied by a constant factor. In addition, the scattering diagram and the fit of pure silica ($\Phi=100 \text{ vol \%}=1$) are depicted. The dotted lines illustrate how the individual levels contribute to the full model. The fitting curves, representing a joint fit, result in a radius of gyration $r_g=8.7 \pm 0.1 \text{ nm}$, hence a radius $r=11.2 \pm 0.1 \text{ nm}$, and a surface fractal dimension $d_s=2.00 \pm 0.01$.

Furthermore, in the case of the composites the unified fit

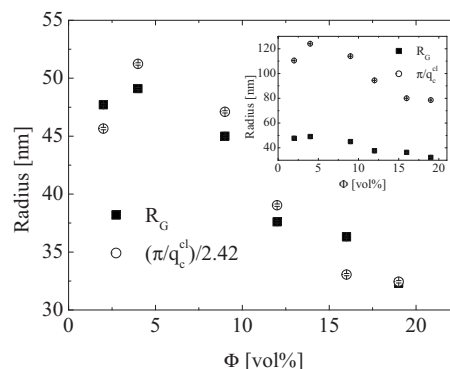


FIG. 2. Radius of the clusters as obtained by the fit of the unified model of Beaucage R_g , compared with the value obtained using π/q_c and divided by a factor of 2.42, cf. text. The inset compares the original values.

provides a mass fractal dimension $d_f=2.41 \pm 0.01$. In contrast, a value $d_f=1.68 \pm 0.01$ is observed for pure silica. All the diagrams (composites and pure silica) are fitted with $B/GR_g^4=5.3 \pm 0.3$ and $B_1/G_1=(1.48 \pm 0.05)10^{-3} \text{ nm}^{-4}$. As depicted in Fig. 2 the radius of gyration of the clusters depends on the filler fraction.

Additionally, to extract the diameters of the primary particles and the clusters, the crossovers themselves were evaluated. In order to obtain their positions q_c , the diagrams can be displayed in a Kratky-like plot as described by Ehrburger-Dolle *et al.*¹⁰ In this representation, the crossovers appear as maxima which can then be fitted by Gaussian interpolation functions and by that means q_c^{prim} and later q_c^{cl} were determined. In the case of the primary particles $\pi/q_c^{\text{prim}}=12.1 \pm 0.1 \text{ nm}$ was obtained. The size of the clusters as obtained from π/q_c^{cl} is displayed in Fig. 2. Between the value from the Beaucage fit and from q_c^{cl} a mean ratio of $(\pi/q_c)/R_g=2.42 \pm 0.1$ is obtained. After dividing (π/q_c) by 2.42 the dependency on the filler fraction is virtually identical.

In the case of the pure powder there is no crossover visible. Therefore, an accurate determination of R_g is not possible. However, by using the Beaucage model function at least a minimum size of 100 nm is estimated, which agrees with the literature²⁷ reporting experiments on similar silica particles.

In the case of the composites at the small q -values a third range appears. Although it seems to be that the slope decreases with increasing filler fraction, the limited low q -range did not allow to fully characterize the larger clusters. Because of the missing crossover, it is evident that their size cannot be determined. However, deviations from a linear decay due to the fractal nature of the clusters even do not allow to extract a trustworthy value reflecting the fractal dimension.²⁸ Since it is possible that the data at lowest q -values suggest a situation which does not reflect the true physical picture, the values are not presented and in particular no discussion is attempted below.

The aggregation number N , i.e., the average number of primary particles in the clusters, can be calculated using several definitions, e.g., some of them are described in Refs. 29 and 30. Three of them [$N=(R_g/R_{g1})^{d_f}$, $N=G_2/G_1$, and $N=(q_c^{\text{prim}}/q_c^{\text{cl}})^{d_f}$] are depicted in Fig. 3, where the last relation

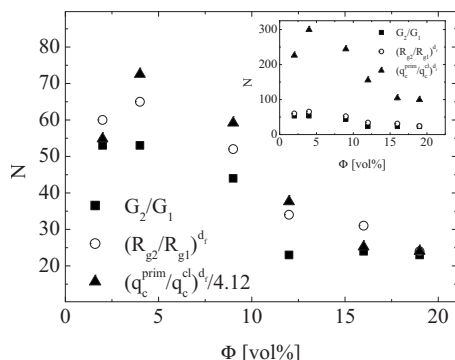


FIG. 3. Aggregation number as obtained by different definitions as a function of the filler fraction Φ . N derived from the crossover is divided by a factor of 4.12, the inset shows the original data.

is a consequence of $R_g \propto 1/q_c$. After dividing the aggregation number derived from the crossover by 4.12, the dependency from Φ as obtained by the different definitions is virtually identical. Using the estimated minimum cluster size, for the pure powder a minimum aggregation number $N=60$ is obtained.

In Ref. 20 the three dimensional structure of a silica cluster was revealed by three dimensional electron transmission microscopy. There it has been shown that the cluster is almost spherically symmetric characterized by its semiaxes $2a \times 2b \times 2c = 120 \times 150 \times 115 \text{ nm}^3$. If one assumes the cluster is fully spherically symmetric this gives a perimeter radius of about 80 nm. Using Eqs. (4) and (5) provides radii of gyration of 54 and 49 nm, respectively. In comparison to the 2 vol % silica sample, the cluster is slightly larger. This observation agrees very well with the larger clusters observed in the scattering experiments on the pure silica powder. In particular the mass fractal dimension of 1.7 from the microscopy experiment agrees very well with the scattering experiment on the powder ($d_f=1.68$). From the microscopy experiment an approximate number of primary particles in the cluster of 34–56 can be calculated, which is similar to $N=60$ obtained by the scattering experiment on the powder.

We now want to interpret the results. Let us first summarize the experimental facts: r , r_g , π/q_c^{prim} , R_g , π/q_c^{cl} , and N are determined by different methods. (i) The absolute values obtained by the individual methods are different. (ii) For the primary particles, it is observed that r , r_g , and d_s do not depend on the silica fraction. In the case of the clusters, R_g and π/q_c^{cl} depend on Φ , but d_f is constant. These results are independent from the analysis technique. In particular, both R_g and N decrease with increasing Φ , except at the low concentrations.

The task is now to understand the differences, as well as the physical dependency on the filler fraction. Let us first address the possible differences obtained by applying the different techniques. The crossover yields $\pi/q_c^{\text{prim}} = 12.1 \pm 0.1 \text{ nm}$. Since π/q_c represents a perimeter radius this value has to be compared with the radius calculated from the fit with the unified model $r = 11.2 \pm 0.1 \text{ nm}$. Considering the different extraction methods, and the values from TEM measurements provided in the sample section, these values are virtually identical and possible origins of the slight dif-

ference need not to be discussed. In the case of the cluster, there is a ratio of the radius of gyration R_g obtained with the Beaucage model and the value from π/q_c of about 2.42. By Eqs. (4) and (5), ratios of $R/R_g=1.83$ and $R/R_g=2$ are obtained, respectively. Obviously, besides d_f , the model itself influences the value of the extracted perimeter radius. Therefore, we conclude that the differences are due to a missing general relationship between the perimeter radius and the radius of gyration, and not due to the different methods of determining the radius. This argument is supported by the dependency on Φ which is virtually identical. It should be added that the similar values of d_f and the ratio may be purely coincidental and no further attempt is made to correlate them.

Hereafter, only the relative changes, e.g., with respect to the $\Phi=2 \text{ vol \%}$ sample, are discussed. By that means both methods reveal the same dependency from the filler fraction and a discussion is possible without losing generality.

The primary particles consist of chemically bonded SiO_2 -molecules and thus it is not expected that forces, e.g., appearing during the mechanical mixing process, are able to crack them. There is no reason why the diameter and the surface fractal dimension of the primary particles should be changed, but in particular no dependency on the filler fraction is expected.

In the case of the clusters, the radius and the aggregation number N depend on Φ . d_f of silica in the composite does not change, but a very large difference is obtained in comparison to the silica powder. First, the different mass fractal dimension of the pure silica ($d_f=1.68$), and of the silica in the composite ($d_f=2.41$), should be addressed. If the pure silica and the silica in the composite are considered to be independent, then diffusion limited aggregation (DLA) $d_f=1.7$ (Ref. 29) and diffusion limited cluster-monomer aggregation within the model of Witten and Sander,³¹ respectively, are possible explanations for the obtained values. However, obviously because of the mixing process the silica shrinks and the mass fractal dimension increases. By that means it is unclear, whether a silica cluster grown by the DLA is simply restructured, or shrunk to a minimum size and then regrown by diffusion limited cluster-monomer aggregation. A clarification of this issue would be possible only by *in situ* monitoring the clusters during the mixing process and is therefore not possible within the present work.

Since the experimental results give evidence that the cluster size is decreased at least by a factor of 2.9, in the following the task is to clarify the question whether forces occurring during the mixing process would be responsible. Recently, it was shown by TEM, e.g., Ref. 32, and by X-ray^{33,34} experiments that the shape of silica clusters can be changed by external forces. In particular, the size of the objects can be changed, e.g., Refs. 32–36, and may be accompanied by a decrease of the mean number of primary particles in the clusters.^{32,34} By that means the external forces compact and break the clusters. Ehrburger and Lahaye³⁶ measured the pressure P transmitted by silica samples during low speed uniaxial compaction as a function of the volume

fraction Φ . For the precipitated silica, with a diameter of 17 nm, they identified two different power laws for $P(\Phi)$ below and above $\Phi \approx 0.13$.

One has to ask whether differences in the microscopic structure in the case of the silica composites are related to a similar phenomenon. This would lead to the simple working hypothesis. (i) There exist external forces because of the mixing of the sample. By that means the cluster size may be decreased. (ii) An internal contribution is possible if the silica clusters are close enough to mutually transmit the external forces from the mixer. (iii) A second internal contribution is possible because of polymer-filler interactions, bridging forces between much longer distances than in the case of the contribution (ii).

Since the surface of the silica particles is not modified adsorption of chains is possible. Therefore, if the silica fraction is very low, both (i) and (iii) possibly influence the observations. However, without changing the strength of the adsorption of the polymer by a modification of the silica surface or by changing the polymer, both contributions are indistinguishable. Hence, only (i) and (ii) are discussed hereafter and (iii) is postponed to future studies. But then the question has to be accessed, how these first two arguments lead to different structures at the microscopic length scale and whether the experiments are able to identify them. In order to clarify this issue the limiting concentration Φ_c has to be determined when the silica cluster is in contact. For the following discussion it seems to be appropriate to assume that the percolation threshold concentration Φ_c represents this value. Since silica is an electrical insulator it is difficult to determine a precise value. However, it can be at least roughly defined by the Young's modulus at small strain in the linear region.³⁷ By that means a percolation threshold $\Phi_c \approx 7.6$ vol % is obtained. Very recently, Kato *et al.*¹⁹ succeeded in measuring indeed the percolation threshold by conductivity measurements. The authors assumed that the conductivity arises from the residual moisture in the hydroxyl functional groups (silanol) covering the silica surface and thus representing the silica particles. By that means a threshold value of around 9 vol % (20 phr) was observed. In addition, they reported a percolating network at larger silica fractions [around 12 vol % (30 phr) and above]. The authors were able to relate these results to the distance of the clusters, measured by electron tomography. In comparison to the silica studied in the present work, at least $\Phi=2$ and 5 vol % are below and $\Phi=12$ –19 vol % are above the percolation threshold. Therefore, at least in a first approximation, at $\Phi=2$, 5, and 9 vol % the particle fraction is low enough that the mutual interaction should play a minor role. Furthermore, the mixing time of the samples was kept constant. By that means in the low Φ -range the cluster radius should not depend on the silica fraction, and this is probably the reason why no systematic dependency is observed there.

At the larger silica fractions a systematic decrease of the radius with Φ is observed. The work of Kato *et al.*¹⁹ suggests a linear decrease of the distance between the clusters at this fraction. This agrees nicely with the approximately linear decrease of the cluster size.

By that means it can be concluded that above the perco-

lation threshold the cluster size is additionally reduced by the clusters which are close enough to mutually transmit the external forces from the mixer. Below Φ_c solely the forces due to the mixer are responsible.

Almost the same Φ -dependency is observed for the aggregation number. Since the mass fractal dimension in the composite is constant, it can be concluded that the decrease of the size is due to breakage of the clusters or due to the rupture of smaller parts of the cluster. Clearly because of mixing the silica with the polymer the mass fractal dimension increases, and by that means the cluster is more compact if compared to the pure powder. Schaefer *et al.*²⁷ report measurements on precipitated silica. By combining different techniques they obtained a crossover at $q_c=0.01$ nm⁻¹. This is in agreement with the size of the clusters in the powder reported above. Furthermore, the number of primary particles found in the microscopy (34–56) and the scattering (60) experiment on the pure silica suggest that at first the cluster size is decreased by compaction. In the case of the results obtained by the scattering experiments it provides a minimum value, and therefore most likely breakage and rupture effects additionally contribute.

The mass fractal dimension $d_f=2.41$ seems to be a value at which no further increase occurs. This assumption is supported by experiments of Schaefer *et al.*²⁷ They report $d_f=2.4$ –2.5 as obtained by scattering experiments on pure precipitated silica and silica dispersed in an elastomer. At the first glance this behavior confirms the idea of robust aggregates. However, as shown by Fig. 2, the cluster size systematically decreases. Therefore, we conclude that the objects observed in the intermediate region of the scattering diagrams are weakly bonded clusters and not aggregates. However, because of the results presented above, one can conclude that the aggregates have a maximum radius of gyration of about 32 nm and consist of a maximum number of 25 particles. In particular, by increasing the silica fraction to much higher values than those studied by the present work, and by that means increasing the mutual forces between the clusters, most likely a minimum size which cannot decrease below a lower threshold would be observed. Therefore, future studies are necessary to clearly determine the size of aggregates and the related number of primary particles.

Furthermore, the scattering diagrams demonstrate that the cluster radius and the mass fractal dimension are not necessarily coupled. At the first glance, it seems to be astonishing why the diameter changes, but not the mass fractal dimension. However, this can be simply illustrated using a homogeneous sphere. This object has a mass fractal dimension $d_f=3$. If the sphere is broken in two parts with a finite size, the average size is smaller if compared to the original sphere. However, this process does not change the mass fractal dimension. This can be generalized to the case of fractals.²³ If the fractal growth is limited by length-scale dependent obstacles, a finite length not related to the growth process itself is introduced. If the type of the growth process is suitably changed after passing the obstacle, it is reflected by a different fractal dimension. In that case the associated correlation function, and hence the scattering diagram, exhibits a crossover in which position is determined solely by

the obstacles and not by the growth process. Obviously due to the mixing process this boundary is shifted to smaller length scales and by that means in accordance with a decrease of the cluster size. If, in the case of silica in rubber, one cluster is considered in the mean field of the surrounding clusters, the obstacles become closer with increasing filler fraction. By that means the decrease of the cluster radius is expected from the theory of fractals whose size is limited because of obstacles.

V. CONCLUSION

Silica filled rubber as a function of the filler fraction was studied by means of small-angle X-ray scattering experiments. The size and the surface fractal dimension of the primary particles do not depend on the filler fraction. The cluster size changes with the filler fraction. It was demonstrated that this is related to the distance between the silica clusters. In particular, it was shown that above the percolation threshold the filler-filler interactions decrease the size as a function of the filler fraction. Below the percolation threshold the filler-filler interactions play a minor role. However, in order to distinguish between external mixer and polymer-filler interactions, further studies are necessary, where the surface of the particles is modified and/or the polymer is varied. Such experiments could be accompanied by studying very low filler concentrations in detail. This would provide an appropriate way to separate the direct mixer and polymer-filler mediated forces. Furthermore, samples with a very high filler content would provide access to higher forces and by that means possibly allow to study the aggregate level in detail. Although there is general agreement on the existence of aggregates, their size and aggregation number are not sufficiently characterized at present. This would be very important, e.g., to predict the percolation threshold, the mechanical properties of composites, etc. From the fundamental view, *in situ* experiments, where silica is monitored by X-rays during the mixing process, would provide very important information, whether silica is regrown in the polymer matrix by another process or simply generated by shrinking the DLA cluster of the silica powder. Of course, monitoring the precipitation process prior would provide access whether the DLA process is responsible for the mass fractal dimension of the pure silica.

ACKNOWLEDGMENTS

We are grateful to the HASYLAB/DESY (Hamburg, Germany) for the beam time on BW4 and for the financial support and to the beam line staff, R. Döhrmann, M. Dommach, and Rainer Gehrke, for help and technical assistance.

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