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Revisiting Silica Networks by Small-angle Neutron Scattering and Synchrotron Radiation X-ray Imaging Techniques

Xin-Wei Kang^a, Dong Liu^b, Ping Zhang^a, Ming Kang^a, Feng Chen^a, Qing-Xi Yuan^c, Xiu-Li Zhao^d, Ying-Ze Song^{a*}, and Li-Xian Song^{a*}

^a State Key Laboratory of Environment-Friendly Energy Materials, Southwest University of Science and Technology, Mianyang 621010, China

^b Key Laboratory of Neutron Physics, Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang 621999, China

^c Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

^d Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang 621900, China

Electronic Supplementary Information

Abstract The silicone rubber composites present remarkable mechanical properties due to the double network structure constructed with molecular network of matrix and filler network of silica. Nevertheless, the filler network structure and corresponding reinforcement mechanism are still under debate and need to be further probed with the aid of applicative advanced analysis techniques. Herein, small-angle neutron scattering (SANS) and synchrotron radiation X-ray nano-computed tomography (Nano-CT) techniques are employed to explore the evolution of filler networks of fumed, precipitated and sol-gel silica, respectively. Our studying results reveal the formation of filler network constructed by the interconnecting of branched silica aggregates. And the silica with highly associated structure, pertaining to amorphous morphology, small size, and large surface area, presents short distance and effective molecular chain bridge between aggregates, thus forming strong and steady filler networks. This work would provide deep-seated revisiting of filler networks and corresponding reinforcement mechanism and offer guidance for optimizing the mechanical properties of silicone rubber.

Keywords Silica networks; Reinforcement mechanism; SANS; Nano-CT

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INTRODUCTION

Silicone rubber displays superior characteristics involving high permeability, thermal stability, and resistance properties under the conditions of oxidation, corrosion, or radiation.^[1,2] However, in a complex external field, the structural changes of silicone rubber networks involving transformation, destruction, and rearrangement can result in macro-mechanical behaviors such as relaxation, creep, and fracture, hence leading to inferior mechanical performances.^[3–5] To tackle this issue, various inorganic fillers such as carbon-based materials, silica, and metal oxides are widely employed to reinforce the silicone rubber products.^[6–10]

Owing to its tailorable morphology, high surface area, and controllable number of hydroxyl groups, silica favorably synergizes the bifunctionality of physical and chemical reinforcement, implying more promising applications in the field of reinforcement in contrast with other fillers.^[11–13] Our recent

work confirmed the addition of silica into silicone rubber could toughen the matrix by three magnitudes, which was far larger than other nanofiller-rubber systems.^[14] To further understand the reinforcement mechanism of silica and optimize the mechanical properties of silicone rubber products, tremendous efforts have been exerted thus far. According to the percolation theory, when the content of filler reaches its percolation value, filler aggregates in the rubber matrix attach to generate a long-range coupling across the whole system, leading to the formation of filler network.^[15–19] The fractal filler network can increase the effective volume fraction of the solid reinforcing phase to maintain strain by blocking or shielding a part of polymer volume.^[20] In addition, the interaction between silica and rubber can induce the formation of bound rubber on the surface of filler particles and thus slow down the dynamics behavior of rubber chains, enhancing the mechanical properties of rubber.^[21–26] The comprehensive regulation of silica structure, mainly pertaining to morphology, size, and surface area, has produced critical influence on the formation of strong and steady filler networks.^[27–29] In light of this, developing state-of-the-art measurements, in combination with systematic modeling toolsets, would be the key to in-depth exploration of silica networks and revisit of

* Corresponding authors, E-mail: yzsong@swust.edu.cn (Y.Z.S.)

E-mail: songlixian@swust.edu.cn (L.X.S.)

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the corresponding reinforcement mechanism.

Recently, the imaging techniques such as atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) have been widely employed to evaluate the dispersion of silica in silicone rubber matrix.^[30–32] Although the dispersion state can reflect the surface activity of silica and its interaction with silicone rubber to a certain extent, it is still insufficient to fully detect the filler networks.^[33–35] The dynamic rheological measurements have been extensively applied to indirectly probe filler networks.^[36–38] For instance, dynamic mechanical analysis (DMA) is subject to oscillatory torsion under a controllable frequency, amplitude, and temperature, offering an indirect verification of the filler networks.^[39,40] However, these dynamic rheological routes are still limited from direct depiction of the filler networks. Therefore, developing advanced dynamic rheological routes to directly probe the filler networks is imperative and meaningful. More recently, a series of advanced techniques such as small-angle neutron scattering (SANS)^[22,41–46] and synchrotron radiation X-ray nano-computed tomography (Nano-CT)^[14,47–49] have served as emerging toolsets to probe the rheology of composites. Moreover, SANS has showed its advantage in evaluating the state of fillers with size of less than 100 nm in matrix. And Nano-CT has been used to depict the spatial distribution of fillers with size of more than 100 nm in matrix. Nevertheless, owing to the multiscale distribution of fillers from nanometers to micrometers in matrix,^[50–52] the separate application of SANS and Nano-CT cannot completely detect the practical dispersion of fillers. Along this line, the combination of SANS and Nano-CT maintains the chemical composition of the composites and can be expected to offer an initial contrast variation route to directly extract the reliable details on multiscale distribution of fillers.

In this contribution, we develop a synergistic analysis strategy, based on SANS, Nano-CT, and in operando rheology measurements to disclose the filler network and corresponding reinforcement mechanism of silica. Our practical experimentations reveal that the silica with highly associated structure, pertaining to amorphous morphology, small size, and large surface area, exhibits short distance and effective molecular chain bridge between aggregates, hence generating strong and steady filler networks. As a result, silica with the highly associated structure more effectively enhances the mechanical properties of silicone rubber in contrast with silica of low association. The proposed synergistic analysis strategy combines the merits of SANS and Nano-CT characterizations, providing a feasible route to explore the filler networks and corresponding reinforcement mechanism.

EXPERIMENTAL

Materials

Methyl vinyl silicone rubber (type: 110-2) was purchased from Zhejiang Xin'an Chemical Group Co., Ltd. (China) and dicumyl peroxide (DCP) was from Chengdu Kelong Chemical Reagent Industry (China). Hydroxyl silicone oil (type: GY-209-3) was provided by Chenguang Research Institute of Chemical Industry, China. Fumed silica (type: A200) was purchased from Dugessa Co., Ltd. (Germany) and precipitated silica (type: Z142)

was from Qingdao Rhodia Co., Ltd. (China). Sol-gel silica was obtained from Technical Institute of Physics and Chemistry, CAS.

Preparation of Silicone Rubber Composites

Silicone rubber compounds were first formulated by stepwise incorporation and mixing of methyl vinyl silicone rubber, silica, and hydroxyl silicone oil with a mass ratio of 100:40:8 in an internal mixer at 105 °C for 30 min. Subsequently, 3 wt% of dicumyl peroxide as vulcanization agent was introduced into the compound. The as-prepared compound was placed in a mold and compressed under 20 MPa for 20 min at 160 °C to obtain the final silicone rubber composites. Fumed, precipitated silica and sol-gel silica were denoted as SA, SZ, and SG, and their corresponding silicone rubber composites were also denoted as RA, RZ, and RG, respectively. The pure Silicone rubber was denoted as R.

Characterization and Measurement

Morphologies of silica and silicone rubber composites were observed by Zeiss Libra 200 FE transmission electron microscopy (TEM) and TESCAN MAIA3 scanning electron microscopy (SEM). Diameter distribution profiles of silica particles were collected by a NanoBrook 90Plus particle size analyzer. N₂ adsorption-desorption isotherms of silica were recorded on a NOVA 3000 surface area and pore analyzer. In operando rheological curves of samples were tested by a RPA 2000 rubber process analyzer at 160 °C. Mechanical properties of samples were tested by a TA RSA-G2 solids analyzer and refer to GB/T 528-2009.

SANS measurement was performed on the SANS-Suanni spectrometer at China Mianyang Research Reactor (CMRR). The scattering length density (SLD) of two main components are as follows: $D_{\text{PMVS}} = 0.07 \times 10^{10} \text{ cm}^{-2}$, $D_{\text{silica}} = 3.47 \times 10^{10} \text{ cm}^{-2}$. The silica particle was characterized by a reasonable natural neutron contrast in the rubber matrix. Three different setups with sample-to-detector distance $L_2 = 2.5$ and 10.44 m for wavelength $\lambda = 0.53 \text{ nm}$ and $L_2 = 10.44 \text{ m}$ for $\lambda = 1.6 \text{ nm}$ were employed, leading to the measured scattering vector q range of $0.02\text{--}1.3 \text{ nm}^{-1}$. q was obtained by $q = (4\pi/\lambda)\sin(\theta/2)$, where θ was the scattering angle. The current wavelength spread ($\Delta\lambda/\lambda$) was around 18%. In order to extract the scattering information of the sample, scattering of the detector background and the empty cell was also measured. Igor Pro software^[53] was applied to realize 2D to 1D data conversion.

Nano-CT measurement was carried out using transmission hard X-ray microscopy (TXM) on the 4W1A beamline at Beijing Synchrotron Radiation Facility (view field: $60 \mu\text{m} \times 60 \mu\text{m}$, spatial resolution: 60 nm , photon energy: 8 keV). Samples were fixed on a self-made tensile device, and subsequently transferred into the vacuum chamber of the imaging device. The exposure time of each image was set to 15 s , and the computed tomography data were collected in the range of -70° to $+70^\circ$ with the rotation angle interval of 0.5° . The two-dimensional (2D) projections of samples were subsequently reconstructed into three-dimensional (3D) tomograms through a software package which was provided by Xradia XMReconstructor software. Finally, 3D visualization analysis of the tomograms was performed by Avizo Fire VSG software (Visualization Sciences Group, Bordeaux, France).

RESULTS AND DISCUSSION

Figs. 1(a)–(c) exhibit the TEM observation of SG, SZ, and SA, displaying diverse morphologies, diameters, structures, and dispersal states. As illustrated in Fig. 1(a), SG shows a monodisperse spherical morphology and the particle diameter is around 200 nm. Both SZ and SA show typical amorphous morphology and their primary diameters are about 20 and 10 nm, respectively (Fig. S1 in the electronic supplementary information, ESI). The primary SA particles aggregate to form higher 3D branched structure in contrast with SZ (Figs. 1b and 1c). In addition, the TEM images also reveal the rougher surfaces of SA and SZ than that of SG. The N_2 adsorption-desorption isotherms of SG, SZ,

and SA have been further collected. As shown in Figs. 1(d)–1(f), the corresponding pore volume values of SG, SZ, and SA are 0.03, 1.21, and 1.67 $\text{cm}^3\cdot\text{g}^{-1}$, respectively. And the BET surface area of SA is 197.11 $\text{m}^2\cdot\text{g}^{-1}$, which is much higher than those of SZ (145.74 $\text{m}^2\cdot\text{g}^{-1}$) and SG (20.19 $\text{m}^2\cdot\text{g}^{-1}$), providing more abundant active adsorption sites for rubber matrix. Moreover, higher surface activity of silica would result in the formation of amorphous branched network structure. Therefore, the structure degree of silica increased in the order of $\text{SG} < \text{SZ} < \text{SA}$.

In order to reveal the formation of different silica networks in the vulcanization process, the in operando rheological curves of RG, RZ, and RA were collected on a RPA 2000 rubber process analyzer at 160 °C for 30 min. As displayed in

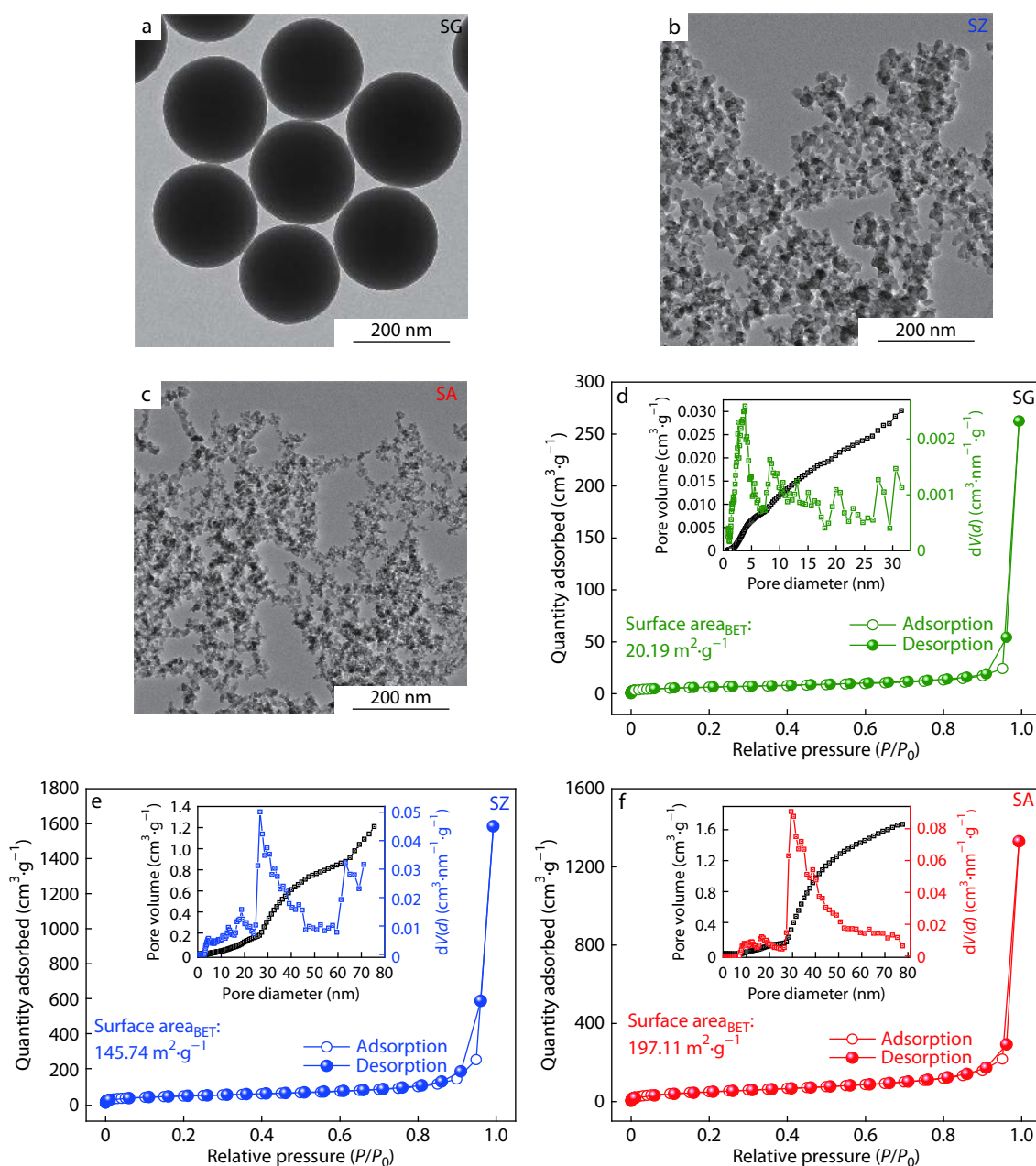


Fig. 1 Characterizations of SG, SZ, and SA. TEM images observed at same magnifications (a–c) and N_2 adsorption-desorption isotherms and corresponding BJH pore diameter distributions of SG, SZ, and SA (d–f).

Fig. 2(a), R, RG, RZ, and RA exhibit torque values (M) of 3.83, 5.37, 10.64, and 12.59 dNm, respectively. In contrast with R and RG, both RA and RZ show larger M values, manifesting their stronger and steadier filler networks. Impressively, due to its highly associated structure degree, SA generated strong interaction with silicone rubber matrix and thus formed the most effective reinforcing networks. Payne effect is used to depict the construction and destruction of filler networks under loading by observing how the dynamic modulus of the filler-incorporated rubber composite relies on the strain amplitude. The Payne effect curves can be explained as follows: (i) in the initial deformation process, the storage modulus (E') is substantially unchanged over a small strain range, and is mainly contributed by filler network structure; (ii) after a period of tension, E' quickly decreases when filler network was destroyed. According to Kraus model, the difference value ($\Delta E'$) of storage modulus between small strain and large strain can reflect the Payne effect of fillers in rubber matrix.^[54] As displayed in Fig. 2(b), the $\Delta E'$ values of RA, RZ, and RG are 5.23, 3.75, and 0.44 MPa, respectively, indicating much stronger Payne effect of RA in comparison with RZ and RG. Moreover, the loss modulus value (E'') of RA is much larger than those of RZ and RG (Fig. 2c). The stronger SA networks suppressed the movement of rubber molecular chain, which caused the outstanding internal friction and energy loss in dynamic stress field, hence enhancing the mechanical prop-

erties of silicone rubber. The engineering stress-strain curves further reveal the superior reinforcing effects of SA compared with SZ and SG (Fig. 2d). To evaluate the toughening effect of SA, SZ, and SG, the fracture energies of RA, RZ, RG, and R were also calculated (Fig. S2 in ESI). RA presents much higher fracture energy value of $33.72 \text{ kJ}\cdot\text{m}^{-2}$ than RZ ($29.02 \text{ kJ}\cdot\text{m}^{-2}$), RG ($0.08 \text{ kJ}\cdot\text{m}^{-2}$), and R ($0.07 \text{ kJ}\cdot\text{m}^{-2}$). The fracture stress values of RA, RZ, RG, and R are 5.22, 4.88, 1.20, and 0.96 MPa, respectively, further corroborating the strong reinforcing effect of SA. In the vulcanizing process, owing to its highly associated structure degree, SA formed more continuous reinforcement interface and more rigid joints in silicone rubber matrix than SZ and SG. The silicone rubber molecular chains were adsorbed on the surface of SA aggregates to generate bound rubber. Subsequently, SA aggregates were bridged with bound rubber to form strong and steady filler networks, thus enhancing the mechanical properties of rubber systems.

In order to further explore the microstructure and distribution of silica in rubber matrix and the influence on the formation of filler network, the aggregation state of silica in the silicone rubber composite system was investigated using SANS technology. The SANS profiles in Fig. 3(a) show a single-scale behavior of SG, while only one break in slope can be observed. Its position, q , is related to the typical interparticle distance ($2R_{cl}$), and locates near $q_{cl} = \pi/R_{cl}$. Different from SG, both SA and SZ exhibit the multiscale behav-

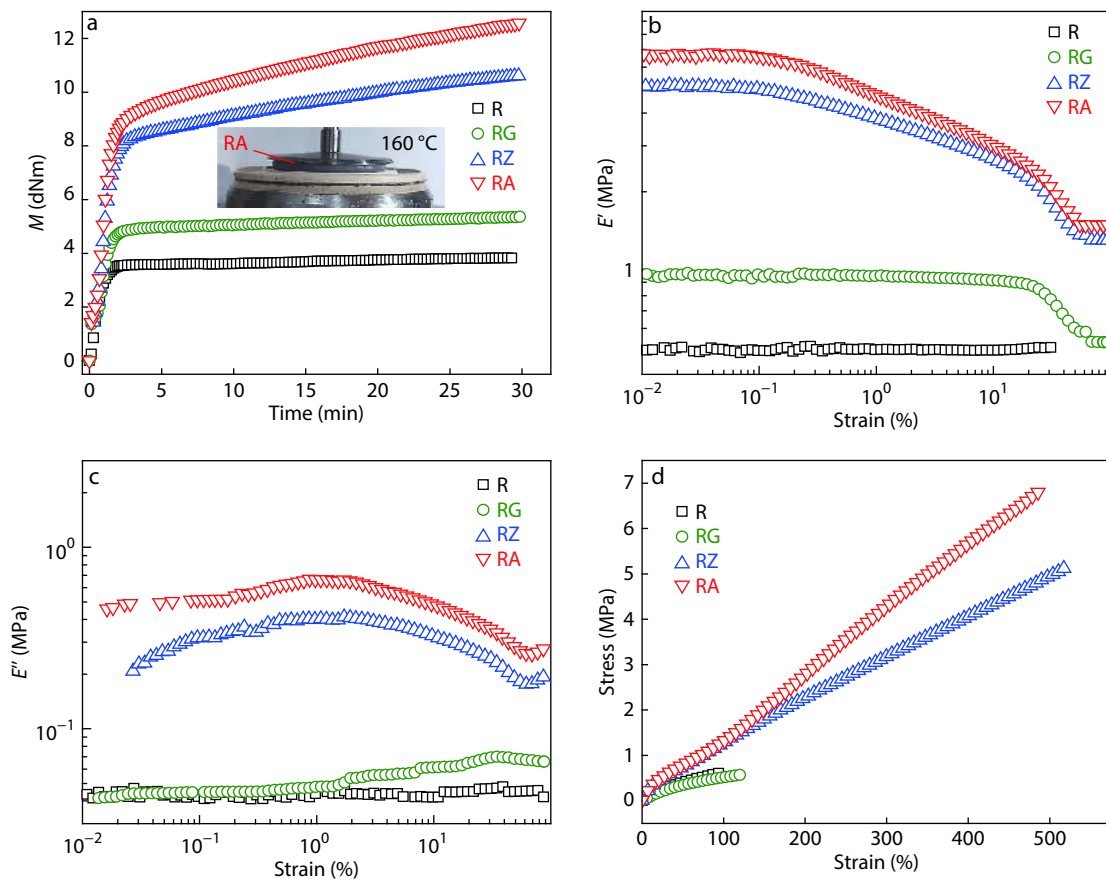


Fig. 2 In operando rheological curves at 160 °C (a), storage modulus-strain curves (b), loss modulus-strain curves (c), and engineering stress-strain curves (d) of RA, RZ, RG, and R.

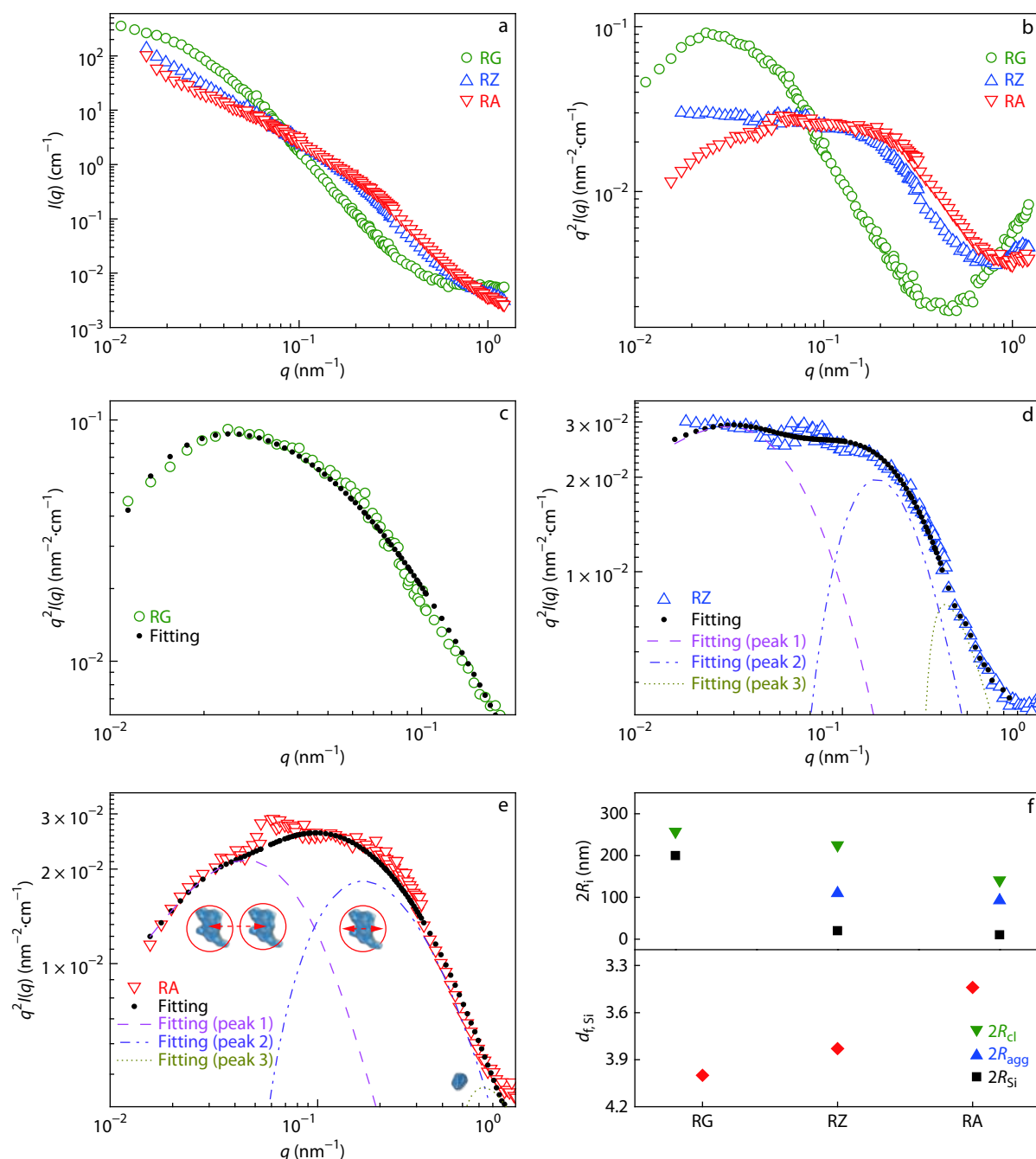


Fig. 3 SANS profiles for silicon rubber incorporated with various silica (a), the same data in the Kratky representation ($q^2 I(q)$ versus q) (b), and RG (c), RZ (d), and RA (e) data with fit by two log-normal functions with parameters q_{agg} and q_{cl} . The parameters $2R_{cl}$ extracted from Kratky plots, $2R_{agg}$ and $d_{f,si}$ values obtained from the Beaucage model fitted (f).

or, where several breaks in slope can be observed. For silica SA and SZ, their breaks in slope locating at high q -region are associated with the typical interparticle distance of the primary particles in contact, and get close to π/R_{Si} . Their breaks in slope in intermediate- q region confirm the existence of small-scale silica aggregates, with radius around $R_{agg} = \pi/q_{agg}$. The low- q scattering law reflects the large-scale fractal organization characteristics of silica aggregates and the average distance in between. To determine the positions of q_{agg} and q_{cl} more accurately, Kratky presentation ($q^2 I(q)$

versus q) is displayed in Fig. 3(b). The breaks in slope were transformed into peak values by counter balancing the power-law reduction. The top peak values in the Kratky plots were fitted by the following lognormal equation ($i = Si, agg, and cl$) (Figs. 3c–3e):^[55]

$$G_i(q) = \frac{A_i}{\sqrt{2\pi}\sigma_i q} \exp \left[-\frac{\ln^2 \left(\frac{q}{q_i} \right)}{2\sigma_i^2} \right] \quad (1a)$$

$$G(q) = G_{\text{Si}}(q) + G_{\text{agg}}(q) + G_{\text{cl}}(q) \quad (1b)$$

where σ is the width parameter and A is the amplitude parameter. In order to achieve more accurate values, the position of the high- q log-normal describing the silica bead q_{Si} is fixed. Fig. 3(f) displays the average distance values determined from the low- q region in Kratky-plot, with the simple correlation $q_{\text{cl}} = \pi/R_{\text{cl}}$. The distance (141 nm) between SA aggregates in rubber matrix is much shorter than those of SZ (225 nm) and SG (258 nm), which provides ampler bridges and more direct connections between interface segments, leading to the generation of denser SA networks.

Beaucage model was employed to further explore the structural characteristics of aggregates and primary particles.^[56] Guinier and Porod regions were modeled as smooth transitions to obtain gyration radius and substructural dimensionality of silica. After subtracting the low- q regions which are associated with the average distance between aggregates, the remaining fraction can be depicted as two-level hierarchical structures (aggregates and primary particles):

$$\begin{aligned} I(q) = & G_{\text{agg}} \exp(-q^2 R_{\text{g,agg}}^2/3) \\ & + B_{\text{agg}} \left[\exp(-q^2 R_{\text{g,agg}}^2/3) \right] \left\{ \left[\text{erf} \left(\frac{q R_{\text{g,agg}}}{\sqrt{6}} \right) \right]^3 / q \right\}^{d_{\text{f,agg}}} \\ & + G_{\text{Si}} \exp(-q^2 R_{\text{g,Si}}^2/3) + B_{\text{Si}} \left\{ \left[\text{erf} \left(\frac{q R_{\text{g,Si}}}{\sqrt{6}} \right) \right]^3 / q \right\}^{d_{\text{f,Si}}} + I_{\text{bkg}} \end{aligned} \quad (2)$$

where G is Guinier scaling factor, B is the Porod scaling factor, R_{g} is the gyration radius, d_{f} is the power law exponent, $\text{erf}()$ is the error function, and I_{bkg} is the background. $R_{\text{g,Si}}$ is set as 4 and 8 nm, as the diameters of primary particle are around 10 and 20 nm for SA and SZ, respectively, in the following Beaucage fitting. By fitting with a model-independent power law equation $I(q) = Aq^{-d_{\text{f}}} + I_{\text{bkg}}$ in the high- q region ($q > 1/R_{\text{Si}}$), d_{f} and I_{bkg} are obtained. d_{f} represents the fractal dimension, the exponent $d_{\text{f}} < 3$ for mass fractals and $3 < d_{\text{f}} < 4$ for surface fractals.^[57] In addition, the possible high and low $R_{\text{g,agg}}$ limits are also constrained. Along this line, the profiles could be well fitted with the Beaucage model (Fig. S3 in ESI). The corresponding fitting parameters are listed in Table S1 (in ESI) and the obtained R_{agg} and $d_{\text{f,Si}}$ are shown in Fig. 3(f). As displayed in Fig. 3(f), the fractal dimension ($d_{\text{f,Si}}$) value of SG is 4, manifesting its smooth surface. SA and SZ give $d_{\text{f,Si}}$ values of 3.44 and 3.83, respectively, reflecting the roughest surface of SA, which is in agreement with TEM results. Moreover, the $d_{\text{f,agg}}$ values of SA and SZ aggregates are 2.37 and 2.33, respectively, suggesting their mass fractal characteristics toward high flocculation and branched fractal in rubber matrix. By assuming the silica as sphere-shaped aggregates, the diameter $2R_{\text{agg}}$ could be calculated with the equation $R_{\text{agg}}^2 = (5/3)R_{\text{g,agg}}^2$.^[58] Thus, the average diameters of SZ and SA aggregates are 109.2 and 91.1 nm, respectively. As only one scatter could be observed in RG sample, the SANS profile was fitted using one-level mode. The average diameter of SG is 206.8 nm, which is in good agreement with the TEM observation of SG.

The SANS results revealed that silica aggregates with highly associated structure possessed small distance in between, implying more efficient connection between neighbor aggregates. Moreover, highly structured silica particles could form

aggregates with mass-fractal characteristics and small sizes, which could provide rubber with ample active adsorptive sites. As a result, the dynamics behavior of rubber molecular chains adsorbed on the surface of silica was effectively retarded, leading to the formation of interfacial layers. Such interfacial layers were favorable for bridge among aggregates and subsequent generation of filler network structure, hence enhancing the mechanical properties of rubber.

The 3D filler network structure was visually observed and quantitatively analyzed using Nano-CT equipment with high spatial resolution and large field of view.^[47] Theoretically, the two-fold density difference between silica and silicone rubber matrix caused different X-ray absorption, hence resulting in their obvious imaging contrast.^[44] To ensure the authenticity of images, the threshold was adjusted until the calculated volume fraction of silica in 3D image was close to the practical value (~15.4%) of samples. The size, position, area, and volume of filler agglomerates were achieved by analyzing the Nano-CT imaging results. Figs. 4(a)–4(c) present the 3D distributions of SG, SZ, and SA aggregates in silicone rubber matrix which is shown in transparency. Different from monodisperse SG, both SA and SZ nanoparticles form aggregates with branched structure and the sizes are in the range of 100–300 nm (Fig. S4 in ESI). In addition, according to the imaging results, the gravity centers of aggregates were connected and skeletonized to generate the silica networks (Fig. S5 in ESI). Fig. 4(d) shows the loose and inhomogeneous filler networks of SG. On the contrary, Figs. 4(e) and 4(f) display the dense and homogeneous filler network distributions of SA and SZ. Impressively, highly structured SA in rubber matrix forms the superior network structure. Key parameters of filler networks were obtained from the 3D imaging and software calculation results involving the number of cross-linking points (N_{p}), average network distance (L), and filler network density (D_{N}). Both N_{p} and D_{N} are critical parameters to evaluate the filler networks.^[14] The N_{p} values of SG, SZ, and SA are 621, 1639, and 1917, respectively. The L values were calculated by equation $L = (V/N_{\text{p}})^{1/3}$ with assumption of the cubic occupation for a single network cross-linked point, where V is the volume of sample. The L values of SG, SZ, and SA are 900, 650, and 600 nm, respectively. The filler network density D_{N} ($D_{\text{N}} \propto 1/L^3$) values of SG, SZ, and SA are 1.41×10^{-6} , 9.81×10^{-6} , and $1.35 \times 10^{-5} \text{ mol}\cdot\text{cm}^{-3}$, respectively. Impressively, SA obtains the highest D_{N} value, further demonstrating its superior filler network structure.

The highly structured SA formed dense and homogeneous networks, which effectively transferred the external stress under deformation. However, it was insufficient for SG to transfer the stress due to its loose and inhomogeneous filler networks. As a result, SA displayed more remarkable reinforcing effect on silicone rubber. The Nano-CT results confirmed the strong and steady networks of highly structured silica. The reasons could be concluded in the following aspects: (i) highly structured silica formed aggregates with branched fractal and small size, offering abundant adsorptive sites for rubber molecular chains; (ii) small average distance between silica aggregates was beneficial to generating chain segments and further producing strong and steady filler networks.

To further verify the distributions of SG, SZ, and SA in silic-

one rubber matrix, SEM was also performed to observe the cryo-fracture failure surfaces of the composites (Fig. S6 in ESI). Fig. S6(a) (in ESI) shows the distribution of individual primary silica spheres in rubber matrix for RG. As displayed in Figs. S6(b) and S6(c) (in ESI), both the branched SA and SZ aggregates uniformly and densely distribute in the silicone rubber matrix, which is in agreement of the SANS and Nano-CT results. Fig. 5 schematically illustrates the networks and corresponding reinforcement mechanism of SG, SZ, and SA on the basis of our systematic experimentations. Silica adsorbs rubber molecular chains to form immobilized rubber composed of tight and loose layer, and the immobilized rubber is so-called “bound rubber”. The content of bound rubber plays a critical role in the construction of filler networks. As displayed in Fig. 5(a), owing to its low association, SG can only form weak particle-particle and particle-rubber interactions, which leads to the inferior filler networks, thus handicapping the

practical application of SG in rubber systems. As displayed in Figs. 5(b) and 5(c), highly structured silica SZ and SA aggregates adsorb and immobilize the rubber molecular chains, retarding the dynamics behavior of rubber and generating superior filler networks. Moreover, due to its highly associated structure, SA presents shorter particle-particle distance and thicker bound layer, which leads to more effective bridges between aggregates, thus forming stronger and more steady filler networks. The reinforcing effects of such highly structured silica on silicone rubber are summarized as follows: (i) highly structured silica could effectively retard the dynamics behavior of rubber molecular chains to produce more bound rubber; (ii) highly structured silica could construct strong and steady silica networks, efficiently transmitting and releasing the stress of the external field. As a result, silica with the highly associated structure effectively enhanced the mechanical properties of silicone rubber.

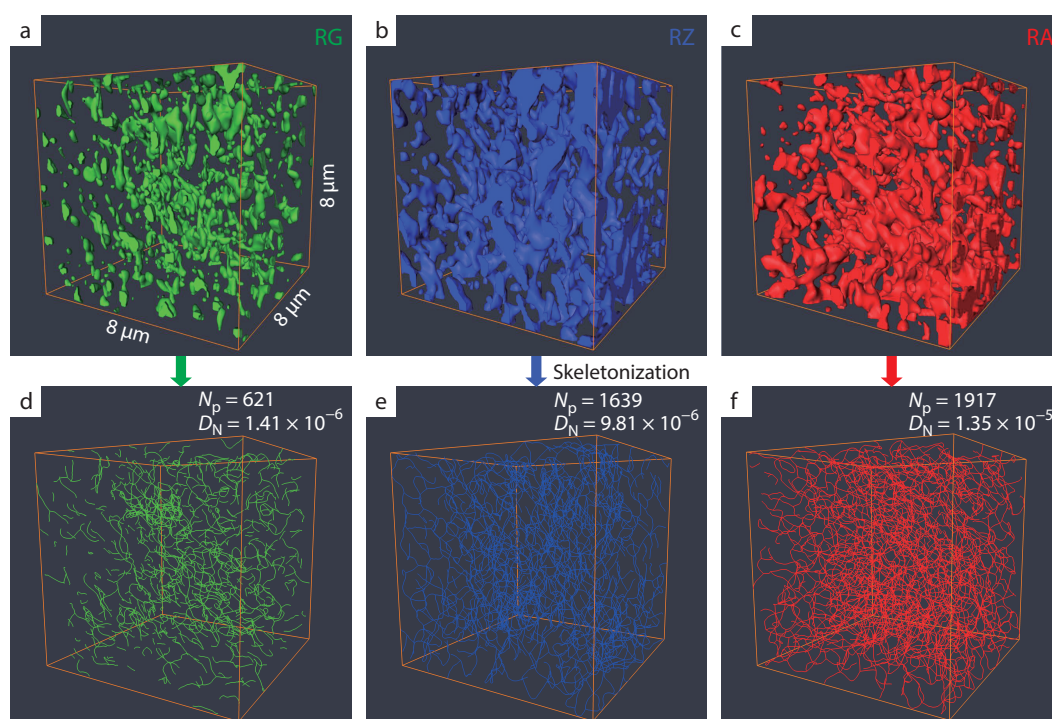


Fig. 4 3D images of RG (a), RZ (b), and RA (c), and network structures of SG (d), SZ (e), and SA (f) by skeletonizing 3D images with the inset showing the number of crosslinking points in filler network (N_p) and filler network density (D_N). The transparent portions are rubber matrix.

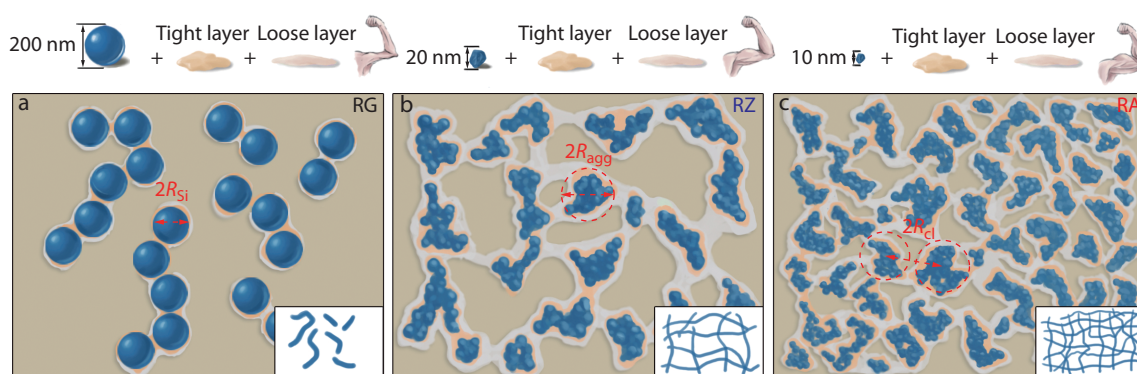


Fig. 5 Schematic illustration of the hierarchical structure and networks of SG (a), SZ (b), and SA (c) in silicone rubber.

CONCLUSIONS

In summary, we have proposed a synergistic analysis strategy, based on in operando rheology as well as SANS and Nano-CT measurements to schematically explore the filler networks and corresponding reinforcement mechanism of silica with different structure degrees. Highly structured silica could effectively adsorb and immobilize the rubber molecular chains, retarding the dynamics behavior of rubber to generate more bound rubber. Moreover, highly structured silica showed shorter particle-particle distance and thicker bound layer, which led to more effective bridges between aggregates, hence forming stronger and more steady filler networks. Such superior filler network structure could efficiently transmit and release the stress of the external field, providing an outstanding reinforcing effect on silicone rubber. With the synergistic analysis strategy, our work performed a systematic exploration on the formation of filler networks and corresponding reinforcing effect, providing an in-depth understanding of reinforcement mechanism and practical guidance for superb silicone rubber product design.

Electronic Supplementary Information

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