

How the Aggregates Determine Bound Rubber Models in Silicone Rubber? A Contrast Matching Neutron Scattering Study

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Electronic Supplementary Information

Abstract The correlation between aggregates and bound rubber structures in silicone rubbers (S(phr)) with various silica fractions (Φ_{Si}) has been investigated by contrast matching small-angle neutron scattering (SANS), swelling kinetics, and low-field nuclear magnetic resonance (NMR). Mixed solvents with deuterated cyclohexane fractions of 4.9% and 53.7% were chosen to match the scattering length densities of the matrix ($S_{MP}(\text{phr})$) and the filler ($S_{MS}(\text{phr})$), respectively. All the data consistently suggest that: (i) There is a critical threshold Φ_{Si}^c between 10 and 30 phr; below Φ_{Si}^c , the isolated aggregates are dominant, while beyond Φ_{Si}^c , some rubber fraction is trapped among the agglomerate; (ii) Φ_{Si} -independent thicknesses around 7.5 nm (NMR) and 8.6 nm (SANS) suggest that the bound rubber formation is determined by inherent properties of the components, and the power-law around 4.2 suggests an exponential changed gradient density of the bound rubber; (iii) $S_{MS}(80)$ presents a bicontinuous bound rubber with three characteristic lengths of 41, 100, and 234 nm. The expanded correlation length, a 20 nm smaller aggregate sizes suggest that such existent bicontinuous network in dry samples with less Φ_{Si} is kind of impacted by swelling. With the obtained bound rubber models, the reinforcing mechanism of filled silicone rubber is elucidated.

Keywords Silicone rubber; Bound rubber structures; Small-angle neutron scattering (SANS); Nuclear magnetic resonance (NMR)

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INTRODUCTION

Over the past several decades, silica-filled silicone rubber, as one of the widely used polymer nanocomposites, has drawn extensive interests due to its outstanding characters, such as excellent mechanical properties, thermal stability, oxidation resistance, radiation resistance, weather resistance.^[1–5] Silica is highly polar and extensively used as filler for reinforcing polysiloxanes, since the mechanical properties of the neat polar elastomers are extremely poor.^[6] Due to the strong filler-rubber interaction, the filler will adsorb the polymer chain to form an interface layer called bound rubber, in which the mobility of chain segments is reduced, and the glass transition temperature (T_g) is increased.^[7] Bound rubber, also defined as the residual gel after a prolonged extraction,^[8] is the transition phase as a dispersed soft shell to bridge the hard filler aggregates and the

even softer polymer matrix. Essentially, it is the filler induced slowed-down of the polymer chains dynamics in the vicinity of the solid particles.^[9,10]

In order to investigate the reinforcing mechanisms of silicone rubber, especially the effect of bound rubber layer, researchers have made great efforts via different methods.^[11–13] Typically, structure parameters such as the size, shape, dispersions of fillers, and modification of fillers can be easily conceived to design various products.^[14] On the other hand, processing parameters such as temperature, strain and strain rate during the mixing processes, storage time, etc. also attract reasonable attention to tune the properties of the materials. Researchers have made extensive endeavors to establish the correlation between the hierarchical structures and the macroscopic properties of the composites.^[15–17] To date, descriptions of the filler structures and their aggregates are relatively well-developed. However, structures and mechanisms of the bound rubber are relatively lacking. For designing high-performance silicone rubbers with desired properties, a clear understanding of the bound rubber is the cornerstone to unveil the inherent mechanism of reinforcement. Nuclear magnetic

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resonance (NMR) is extensively used to give access to the amount of immobilized polymer and discern chain dynamics difference to acquire network distribution under various conditions by residual dipole coupling of polymer chain.^[18–23] By using ^1H double-quantum (DQ) NMR, Sawvel *et al.* presented a significant and quantifiable non-ideal silicone network topology.^[21] Papon *et al.* proposed that there exists a gradient of T_g in the vicinity of the solid particles with the intermediate and elastomer components by NMR investigations.^[16] For the community of small-angle scattering (SAS), different incident beams (X-ray or neutron) or the combination have been utilized to gain deep insight into the hierarchical structures of polymeric materials and nanocomposites.^[24–27] Moreover, benefiting from the enormously different neutron scattering length density (SLD) of hydrogen (H) and deuterium (D), the contrast among components in the composites can be tuned, and the small-angle neutron scattering (SANS) is a powerful tool to distinguish such variation of contrast.^[28–32] Specifically, the contrast matching SANS (CM-SANS) method allows people to directly mask unwanted structural information or simplify complex multi-domain soft-matters via H/D exchange.^[33] Recently, we conducted a contrast variation SANS (CV-SANS) method to analyze the microstructures of silicone rubber, and the existence of a ca. 8.5 nm thickness bound rubber layer was presented.^[34] Most recently, a series of silicone rubbers were prepared with various filler fraction (Φ_{Si}) and investigated, different reinforcement effects and filler morphology were found for the high and low Φ_{Si} , respectively.^[35]

In current work, special attention was paid to describing different microstructures of bound rubber models in the silica-filled silicone rubbers with various Φ_{Si} . CM-SANS measurements were conducted with the swelling techniques. The contrast matching points were fulfilled by mixing the hydrogenated and deuterated solvent with specific ratios. In this way, the microstructures of bound rubber with various Φ_{Si} were extracted. Moreover, the content of bound rubber and matrix network distribution of the composite were estimated with NMR measurements for both dry and swollen samples. Furthermore, the swelling is treated as a scenario to mimic the mechanical deformation on the samples. Accordingly, combined with mechanical measurement of previous work,^[35] the effects of filler fraction on the diversity of bound rubber structures, as well as on the difference of inherent mechanism of reinforcement are discussed.

EXPERIMENTAL

Samples

Silica-filled silicone rubbers used in the current work has been described previously.^[35] The rubber matrix is polymethylvinylsiloxane (PMVS, type: 110-2), with a number-average molecular weight and a polydispersity of about 6.0×10^5 g/mol and 2.6, respectively. The vinyl content is 0.16 mol%. Precipitated silica (type: 36-5) with an average primary particle size of about 25 nm was used as the filler, the specific area is in the range of 170–210 m^2/g . High molecular weight hydroxyl silicone oil (HMWHSO, 3 phr (parts per hundred rubber)) was added to improve the compatibility between filler and polymer. The M_n is around 5×10^4 – 2×10^6 g/mol, the hydroxyl content is

about 13%–15%. Triallyl isocyanurate (TAIC, 4 phr) as the radiosensitization agent was added to accelerate the irradiation crosslinking. Composites with various filler fractions (Φ_{Si}) from 5 phr to 80 phr were mixed for 10 min under room temperature and screw speed of 600–800 r/min. The mixtures were kept under quiescent condition for 36 h. After remixed, the composites were molded to plates under pressure of 10–15 MPa. Then the molded plates were irradiated with γ -ray from a ^{60}Co source. The total dose and dose rate were 50 kGy and 100 Gy/min, respectively.

Swelling Experiment

Swelling kinetics of silicone rubbers in hydrogenated cyclohexane (C_6H_{12}) were obtained with gravimetric measurement. The C_6H_{12} (analytical reagent) was purchased from Chengdu Kelong Chemical Reagent Industry, China. The ambient temperature was set to be 25 $^\circ\text{C}$. Weight of dry specimens (W_0), during the swelling (W_t) at suitable intervals and under equilibrium (W_s) were recorded.

Small-angle Neutron Scattering (SANS)

The specimens were swollen by a mixture of C_6H_{12} and deuterated cyclohexane (C_6D_{12}) at 25 $^\circ\text{C}$ in the quartz cell. The C_6D_{12} (D: 99.5%) was purchased from Cambridge Isotope Laboratories, Inc. Table 1 depicts the scattering length density (SLD) for each component. Three different C_6D_{12} fractions of 4.9%, 53.7%, and 100% were chosen to tune the SLD of solvent matrix. 4.9% and 53.7% are the matching point of PMVS and filler silica. For the sake of brevity, the dry sample set and the three sample sets are hereafter referred to as series S(phr), $S_{\text{MP}}(\text{phr})$, $S_{\text{MS}}(\text{phr})$, and $S_{\text{FD}}(\text{phr})$, respectively. After the specimens reaching their equilibrium state, SANS measurements were conducted at the China Mianyang Research Reactor (CMRR), on the SANS-Suanni spectrometer.^[36–38] Four different setups with sample-to-detector distance $\text{SDD}=1.1$ m, 4.3 m, and 10.3 m for wavelength $\lambda=0.53$ nm, and $\text{SDD}=10.3$ m for $\lambda=1.3$ nm were used, resulting in a q range of 0.02 nm^{-1} to 3.0 nm^{-1} . q is the magnitude of the scattering vector defined by $q = (4\pi/\lambda)\sin(\theta/2)$, where θ is the scattering angle. The current wavelength spread ($\Delta\lambda/\lambda$) is $\sim 18\%$.

Table 1 Scattering length density (SLD) of each component used.

Sample	Density (g/cm^3)	SLD (cm^{-2})
Silica	2.2	3.47×10^{10}
Silicone rubber (100% 2Me)	0.99	6.51×10^8
H-cyclohexane (C_6H_{12})	0.779	-2.78×10^9
D-cyclohexane (C_6D_{12})	0.893	6.70×10^{10}
$S_{\text{MS}}(\text{phr})$ (53.7 vol% C_6D_{12})	0.840	3.47×10^{10}
$S_{\text{MP}}(\text{phr})$ (4.9 vol% C_6D_{12})	0.785	6.51×10^8

Low Field ^1H -NMR

Two different pulse sequences were employed to obtain magic-sandwich echo-free induction decay (MSE-FID) and double quantum (DQ) curve on the benchtop Bruker Minispec mq 20 with ^1H -Larmor frequency of 19.95 MHz. The $(\pi)/2$ and π pulses were 2.60 and 5.20 μs , respectively. The pulse length (τ_p) was set to be 2.6 μs with a recycle delay of 5 s. In current work, 40 time points (τ_{DQ}) were used to measure the DQ build up curve with more time points chosen at earlier τ_{DQ} time to increase the reliability of the fitting procedures. And the free induction decay (FID) with magic-sandwich echo (MSE) (to avoid “dead-

time" issue) was employed to acquire MSE-FID curve, the dead time of receiver of the Minispec was $\sim 9 \mu\text{s}$. The ambient temperature was regulated as 25°C by BTV3000 heater with pure nitrogen gas, and the temperature accuracy was controlled within $\pm 0.5 \text{ K}$. The swollen samples were stored on fully deuterated cyclohexane ($100\% \text{ C}_6\text{D}_{12}$) at 25°C more than 24 h to ensure the swelling equilibrium, and the same parameters were used to obtain DQ build up curves.

RESULTS

Swelling Kinetics

The swelling behaviors of silicone rubbers were evaluated via the gravimetric measurement. Fig. 1(a) depicts the swelling ratio $Q = V_s/V_0$ of samples in cyclohexane as a function of time, where V_0 and V_s are the volumes of dry and swollen samples under equilibrium, respectively. The swelling ratio rises sharply in the initial stage. Fig. 1(b) depicts that the swelling ratio decreases monotonically from 6.6 to 2.9 with increasing the Φ_{Si} from 5 phr to 80 phr. Fig. 1(b) also presents the half time of the whole swelling process ($t_{1/2}$) as a function of Φ_{Si} . With increasing the Φ_{Si} from 5 phr to 80 phr, the $t_{1/2}$ decreases from 45.4 min to 22.5 min. However, interestingly, there is a slight upturn from 31.3 min to 34.8 min in the Φ_{Si} range of 40 phr to 60 phr. With further increasing the Φ_{Si} to 80 phr, the $t_{1/2}$ decreases sharply again.

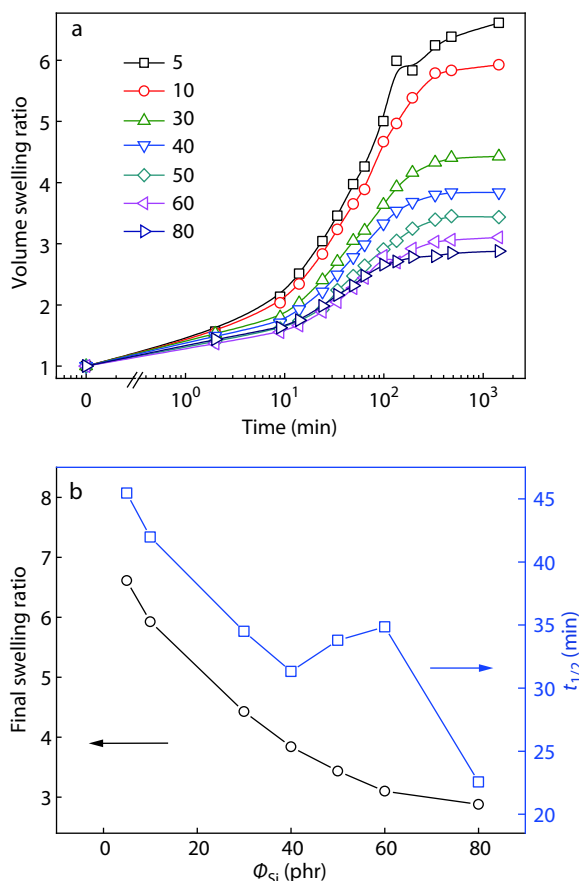


Fig. 1 (a) Swelling kinetics of the silicone rubber in cyclohexane, monitored by gravimetric measurement. (b) Final swelling ratio and half time of the swelling processes versus filler fraction (Φ_{Si}).

Swelling with Fully Deuterated Solvent ($S_{\text{FD}}(\text{phr})$)

First, SANS profiles of series silicone rubber are measured in swollen state in $100\% \text{ C}_6\text{D}_{12}$. Fig. 2 shows that the q dependence, the slopes, and the breaks in slope of each curve for series $S_{\text{FD}}(\text{phr})$ are distinctly different from each other. Interestingly, there is a cross-point around 0.2 nm^{-1} . In the high- q region, the intensity decreases with increasing Φ_{Si} , which suggests that intensity from the polymer network swollen in the C_6D_{12} solvent is dominant. While in the medium- q region, the intensity upturns and increases with increasing the Φ_{Si} , which suggests that the filler aggregates and the bound rubber might contribute more to the intensity. $S_{\text{FD}}(60)$ and $S_{\text{FD}}(80)$ show the intensity decreasing behavior in the low- q region, which might be caused by the repulsive interaction between aggregates and the likely decreasing in aggregates mass.^[15] In a word, it seems that the multi-component systems $S_{\text{FD}}(\text{phr})$ contribute to complicated q -dependences, suggesting the necessity for distinguishing each component of the composites.

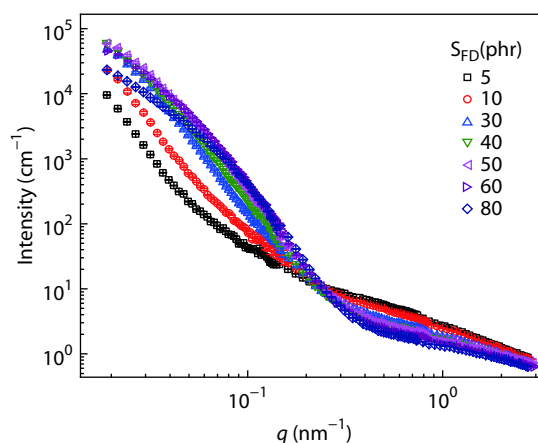


Fig. 2 SANS profiles of silicone rubber swollen by $100\% \text{ C}_6\text{D}_{12}$.

Matching the Polymer Matrix ($S_{\text{MP}}(\text{phr})$)

In order to decompose the hierarchical structures of the sample systems and gain more insight into the materials, especially the bound rubber region, the CM-SANS technique is utilized. First, the mixed solvent with C_6D_{12} fraction of 4.9% (series $S_{\text{MP}}(\text{phr})$) is used to tune the SLD exactly the same as that of the polymer matrix (Table 1). In this way, the information of bound rubber can be masked. Clean morphology of filler network under swollen state can be exclusively highlighted. Comparing the SANS profiles of series $S_{\text{MP}}(\text{phr})$ in Fig. 3(a) with the previous SANS data of dry samples ($S(\text{phr})$),^[35] there are some discrepancies of the q -dependence, the absolute intensity and the q positions of breaks in slope, which might be caused by some form factor and structure factor changes induced by swelling. The $q^2 I(q)$ - q curves of $S_{\text{MP}}(\text{phr})$ are presented in Fig. 3(b). Utilizing the decomposition procedure as previously depicted, three overlapping maxima of each curve in Fig. 3(b) have been fitted using sum of three functions M_{Si} , M_{agg} , and M_{CL} .^[35,39]

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

$$M(q) = M_{\text{Si}}(q) + M_{\text{agg}}(q) + M_{\text{CL}}(q) \quad (2)$$

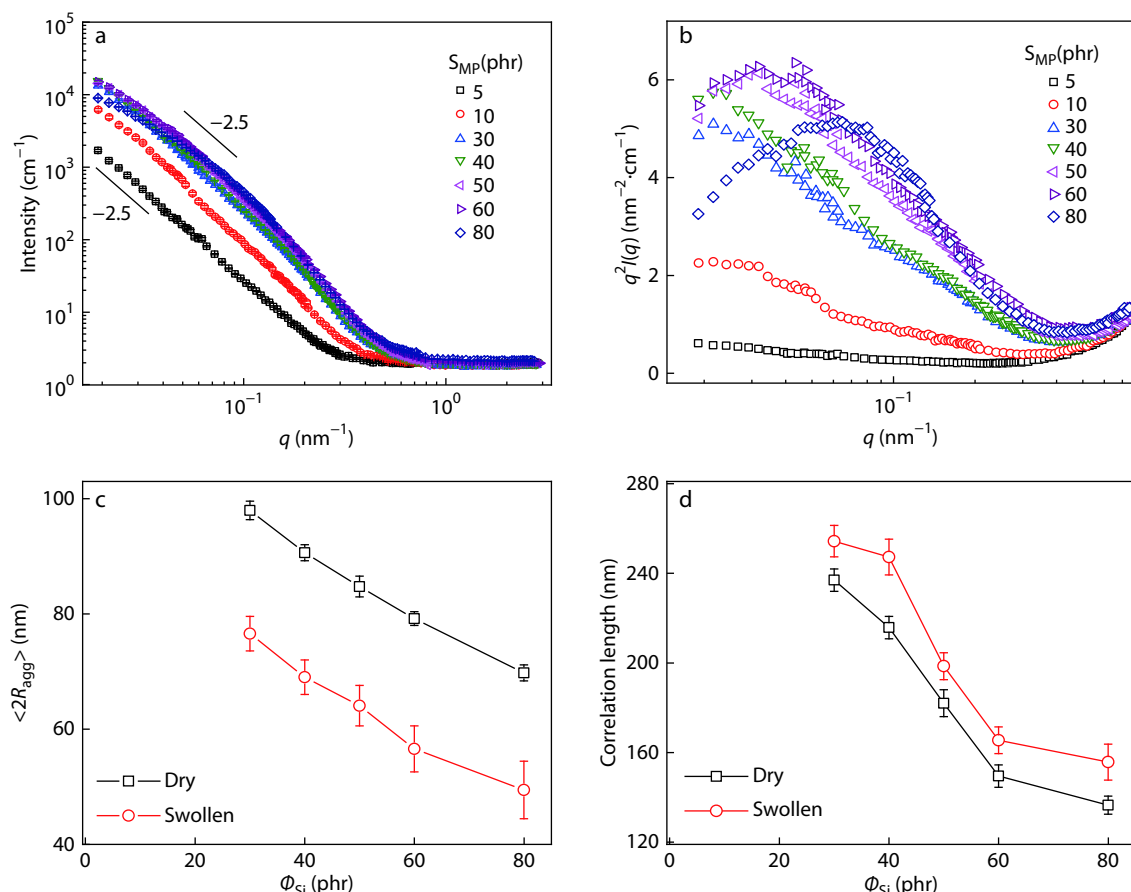


Fig. 3 (a) SANS profiles of silicone rubber swollen by C_6D_{12}/C_6H_{12} mixed solvent with C_6D_{12} fraction of 4.9% (series $S_{MP}(\text{phr})$). The lines represent power-laws $I(q) \propto q^{-\alpha}$ with the α value given. (b) The same data in the Kratky representation. (c) The $\langle 2R_{agg} \rangle$ and (d) the correlation length (L_c) versus Φ_{Si} of dry ($S(\text{phr})$)^[35] and swollen ($S_{MP}(\text{phr})$) samples, determined from the Kratky-plot of SANS data.

Each function describes a log-normal function of position q_{iv} , amplitude A_{iv} and width σ_i (The subscript $i = Si, agg$, and CL represent silica, aggregate, and correlation length, respectively). Figs. 3(c) and 3(d) summarize the aggregate sizes ($\langle 2R_{agg} \rangle$) and correlation length (L_c), respectively, determined from the peaks of Kratky-plot, with the expressions of $q_{CL} = 2\pi/L_c$ and $q_{agg} = 2\pi/\langle 2R_{agg} \rangle$. Similar behavior related to the Φ_{Si} shows that with increasing the Φ_{Si} , both $\langle 2R_{agg} \rangle$ and L_c decrease monotonically. However, as depicted in Figs. 3(c) and 3(d), compared with the dry samples, the swollen samples have relatively small $\langle 2R_{agg} \rangle$ and large L_c . All the $\langle 2R_{agg} \rangle$ in swollen state are about 20 nm smaller than the corresponding dry samples. However, L_c expands within a range from 20 nm to 30 nm. Series $S_{MP}(\text{phr})$ help us to get the information of the filler structure under swollen state exclusively, and as an instruction for further investigation of the bound rubber formation *via* series $S_{MS}(\text{phr})$.

Matching the Filler Silica ($S_{MS}(\text{phr})$)

Further, aiming to investigate the bound rubber models with various Φ_{Si} , the mixed solvent with a C_6D_{12} fraction of 53.7% was used to match the filler silica. Fig. 4(a) presents SANS profiles of series $S_{MS}(\text{phr})$, whose q -dependence is entirely different comparing with that of series $S_{MP}(\text{phr})$ and $S_{FD}(\text{phr})$. First, the absolute intensity decreases obviously. Second, the intensity in

the medium- q region declines distinctly, which might be caused by the matching of the main scatterers silica. Guinier-Porod model is employed to acquire the radius of gyration (R_g) and Power law by:

$$I(q) = \frac{G}{q^s} \exp\left(\frac{-q^2 R_g^2}{3-s}\right) \text{ for } q \leq q_1 \quad (3)$$

$$I(q) = \frac{D}{q^d} \text{ for } q \geq q_1 \quad (4)$$

where q is the scattering variable, d the Porod exponent, s the dimension variable, G the Guinier scale factor, and D the Porod scale factors. q_1 can be calculated by:

$$q_1 = \frac{1}{R_g} \left(\frac{3d}{2} \right)^{1/2} \quad (5)$$

Two Guinier-Porod model was employed to obtain the R_g and d of bound rubber for series $S_{MS}(\text{phr})$. All the experimental data are well fitted with two Guinier-Porod model. $S_{MS}(40)$ in Fig. 4(b) is presented as an example. The Porod exponent and the R_g are the main parameters yielded in region I and region II, respectively. For $S_{MS}(10)$ to $S_{MS}(60)$, s in region II is constant as 2.0, which suggests a lamellar structure. R_g is in the range of 2.3 nm to 2.6 nm. According to the relationship between R_g and a randomly oriented lamella of

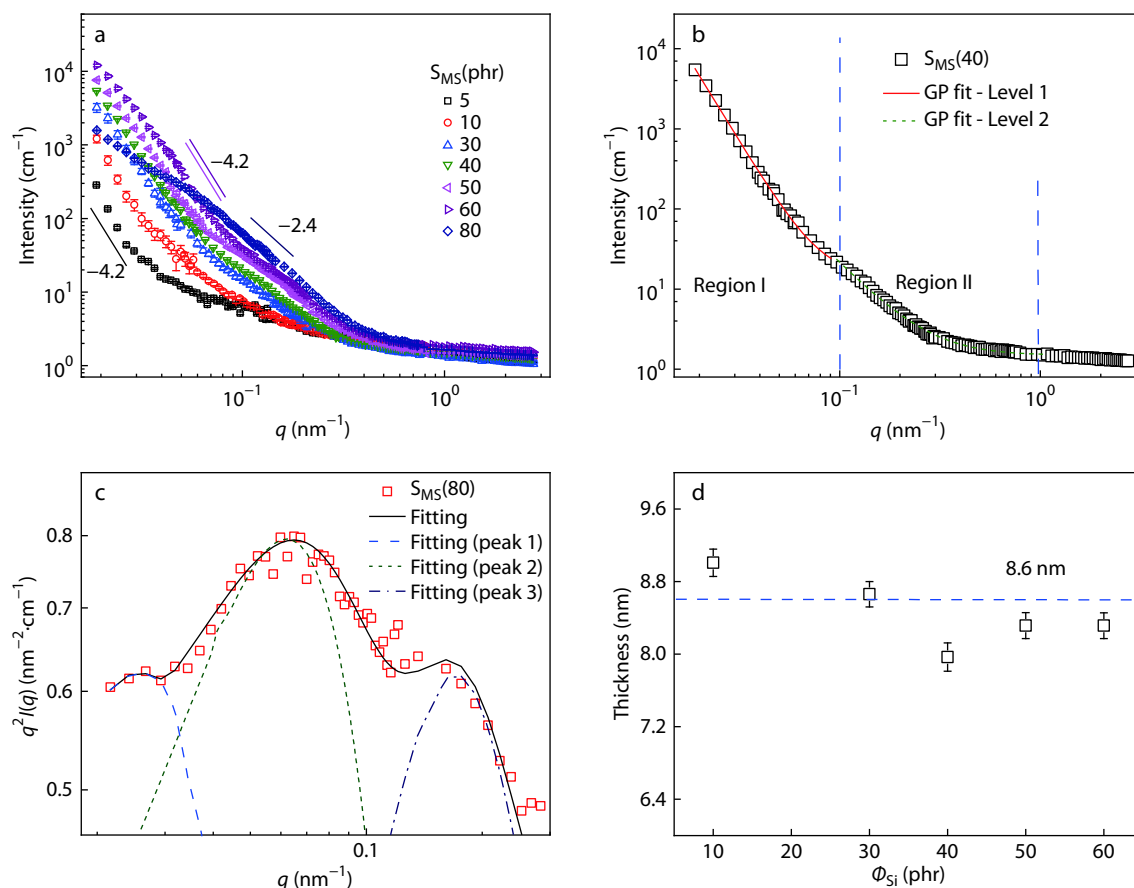


Fig. 4 (a) SANS profiles of silica-filled silicone rubber swollen by C_6D_{12}/C_6H_{12} mixed solvent (series $S_{MS}(phr)$), with C_6D_{12} fraction of 53.7%. The lines represent power-laws $I(q) \propto q^{-a}$ with the a value given. (b) $S_{MS}(40)$ as representative, fitted by two Guinier-Porod model (c) Kratky representation of $S_{MS}(80)$, fitted by sum of log-normal functions. (d) A Φ_{Si} -independent characteristic length around 8.6 nm.

thickness (T):

$$R_g = \frac{T}{\sqrt{12}} \quad (6)$$

The calculated thicknesses of bound rubber are given in Fig. 4(d), which is Φ_{Si} -independent and around 8.0–9.0 nm. The Kratky representation of $S_{MS}(phr)$ is given in Fig. S1 (in the electronic supplementary information, ESI). Interestingly, $S_{MS}(80)$ curve is significantly different, as there are three peaks of $S_{MS}(80)$ at 0.153, 0.0628, and 0.0268 nm^{-1} fitted by sum of log-normal functions, as indicated in Fig. 4(c), corresponding to three character lengths of 41, 100, and 234 nm, respectively.

The three dimensional (3D) structures can be investigated by using the fractal approach on SAS.^[9,40] Note that for power-law dependence, q ranges should be carefully chosen to fall in the windows of $2\pi/D < q < 2\pi/d$, where D is the upper limit for the mass fractal structure and d is the primary unit of the structure. The model-independent power-law equation of $I = Aq^{-a} + B$ is used to fit suitable fractions of the SANS curves. For series $S_{MP}(phr)$, q ranges are chosen between the two breaks in slope which correspond to the size of primary particle and the aggregates (indicated in Fig. 3a). All the a values of series $S_{MP}(phr)$ are in the range of 2 to 3 as presented in Fig. 5, suggesting a mass fractal character of the aggregates, and the fractal dimension is independent of Φ_{Si} . The results

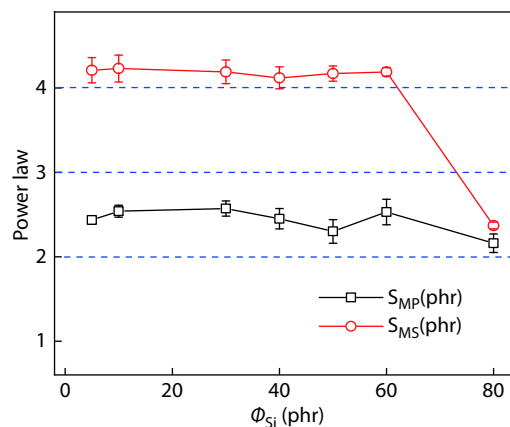


Fig. 5 The a values of series $S_{MP}(phr)$ (square) and $S_{MS}(phr)$ (circle), extracted by power-laws fitting with q range carefully chosen with the restriction of $q \gg 1/D$.

are in accordance with the dry sample as previously discussed.^[35,41] For series $S_{MS}(phr)$, the aggregates are larger than 50 nm as provided by Fig. 3(c). In addition to the bound rubber thickness, the characteristic size is relatively large, and accordingly, the restriction of $q \gg 1/D$ is referred. Moreover, breaks in slope in relatively low- q region are avoided, as indic-

ated in Fig. 4(a). In this way, the α values of series $S_{MS}(\text{phr})$ are extracted in Fig. 5. Interestingly, α values of all the $S_{MS}(\text{phr})$ samples are around 4.2, except for $\alpha=2.4$ of $S_{MS}(80)$. The exponent larger than 4 is assigned to the continuous SLD of the bound rubber region. Ruland^[42] suggested that the SAS intensity can decrease more rapidly than the power-law of q^{-4} when the density (electron density for X-ray and SLD for neutron) change at the surface of a scatterer is continuous. Schmidt *et al.* proposed functions to describe such continuous surfaces by:^[43]

$$I(q) = I_0 q^{-(4+2\beta)} \quad (7)$$

$$\Delta(x) = \Delta_0 (x/a)^\beta \quad (8)$$

where x is the distance perpendicular to the boundary surface, a is the thickness of the boundary layer in which the density changes, and $0 \leq x \leq a$, $0 \leq \beta \leq 1$. In our case, Δ_0 is the constant value of the SLD within the swollen matrix, for points on the boundary (closest to silica) surface, $x=0$ and positive values of x specify points in the bound rubber region. According to Eq. (7), β in swollen samples is about 0.1. The estimation for the SLD evolution in the bound rubber region and the corresponding schematic illustration are presented in Fig. 6. It suggests that the bound rubber layer has a fine structure with exponential changed gradient density. The SLD of the bound rubber changes sharply close to the filler, which already reaches 81%–86% of Δ_0 at the thickness of 1–2 nm, and slowly reaches the Δ_0 for the rest 6.6 nm thickness. As for $S_{MS}(80)$, the α value of 2.3 suggests that the bound rubber layer on the aggregates has the branched structures. Since the 80 phr sample has the smallest aggregate size and the closest correlation length as proposed by our previous work,^[35] the filler network and the rubber network might be assembled to be interpenetrated, with the bound rubber and polymer matrix as the bridge, and be observed within the scope of current q window.

Estimation of Rigid Component and Bound Rubber by MSE-FID

The proton free induction decay (FID) curve is closely related to the chain mobility of rubber matrix. The constraint segmental motion within filler-rubber interface leads to the faster decay of FID, compared with that of near rubber matrix. However, suffering from the inevitable dead time, the signal of the

interface might be largely lost, resulting in the underestimation of bound rubber fraction. The magic-sandwich echo (MSE) sequence is added before detection to recover the lost signal, which fully captures the FID signal of the whole sample.^[18,44] The detail of MSE-FID pulse sequence is given in Fig. S2 (in ESI).

Fig. 7(a) presents MSE-FID curves of the dry series $S(\text{phr})$. The normalized curves show a clear tendency that increasing Φ_{Si} leads to faster decay of the intensity, which suggests the slowing down of chain mobility. As demonstrated with $S(80)$ in Fig. 7(b), the experimental curves are fitted by two-component fitting:^[18]

$$I_0 = A_m \times e^{-\frac{t}{\tau_{\text{mobile}}}} + A_r \times e^{-\frac{t}{\tau_{\text{rigid}}}} \quad (9)$$

where I_0 is an amplitude factor, A_m and A_r are the fraction of the mobile and rigid component, respectively. $A_m + A_r = 1$ since the composites are treated as a two components system containing the mobile and rigid fractions. The fitting parameters with the fitting residual errors are summarized in Table 2. The results of $S(5)$ and $S(10)$ are absent since a two-component fitting is hard to convergence for the relatively low Φ_{Si} . The A_r is regard as an estimated ratio of rigid component.^[44] A_r increases with increasing Φ_{Si} , while τ_{rigid} is constant. Interestingly, normalized with silica volume fraction/surface, A_r/Φ_{Si}^V gives a Φ_{Si} -independent constant value of all the dry samples. Moreover, Saalwächter *et al.*^[45,46] proposed a function to estimate bound rubber thickness by NMR, as:

$$T = \frac{d}{2} \left[\left(\frac{A_r}{\Phi_{Si}^V} + 1 \right)^{1/3} - 1 \right] \quad (10)$$

where d is the silica diameter and Φ_{Si}^V is the silica volume fraction. According to current NMR results, the thicknesses of $S(\text{phr})$ samples are constant around 7.5 nm, as also given in Table 2.

Rubber Matrix Indicated by ^1H DQ NMR

The ^1H DQ NMR (for ^1H DQ NMR pulse sequences, please see Fig. S3 in ESI) method allows the quantification of dipolar coupling interactions between neighboring protons on polymer chains. Due to topological constraints, homonuclear (^1H - ^1H) dipolar was incomplete motional averaging, which is called dipolar coupling interactions. The dipolar coupling interactions that persist are termed as residual dipolar couplings. The

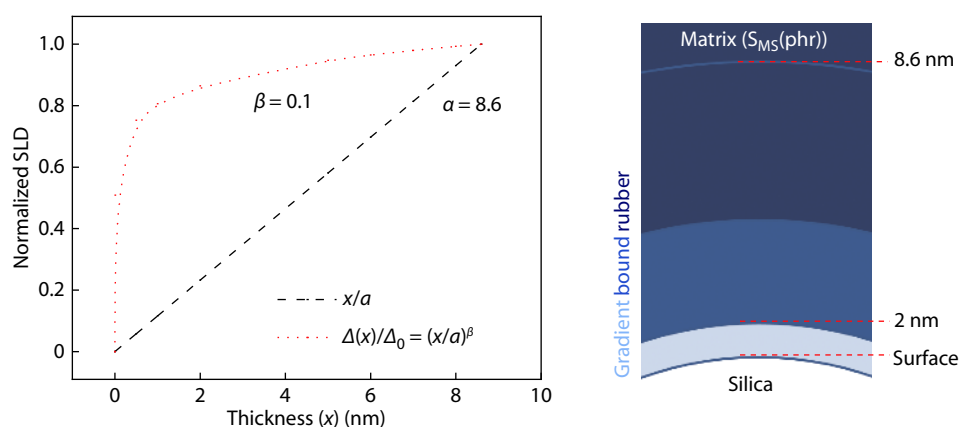


Fig. 6 The estimation of SLD gradient ($\Delta(x)/\Delta_0$) as a function of the thickness (x) of the bound rubber regions (left side) and the schematic illustration of the gradient bound rubber layer (right side).

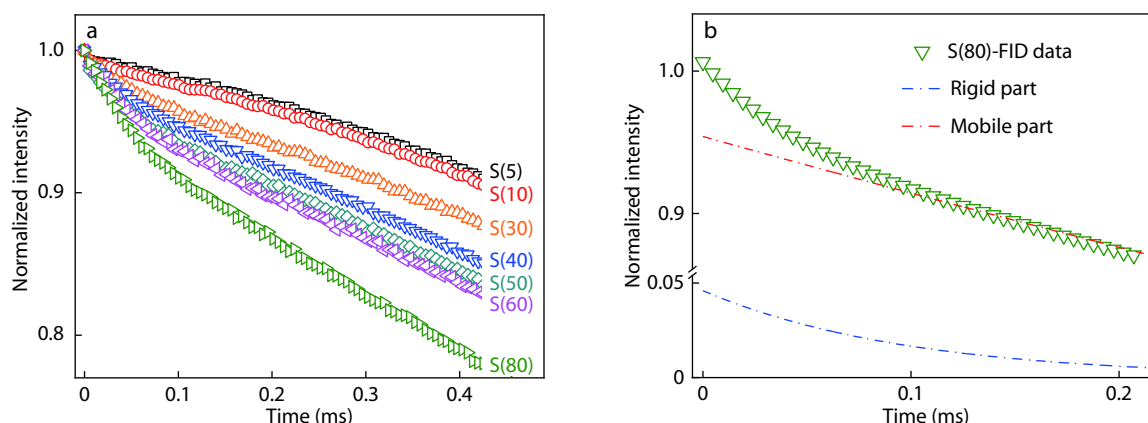


Fig. 7 (a) The MSE-FID curve of each sample, and (b) the representative MSE-FID fitting with S(80) as an example.

Table 2 Fitting parameters of MSE-FID.^a

Sample	Φ_{Si}^v (phr)	Φ_{Si}^v (%)	A_m (%)	A_r (%)	A_r/Φ_{Si}^v	τ_{mobile} (ms)	τ_{rigid} (ms)	T (nm)
S(30)	30	11.9	97.978(56)	2.1902(22)	0.00184	3.7237(95)	0.090512(56)	7.62
S(40)	40	15.3	97.226(23)	2.7803(28)	0.00181	3.5243(76)	0.091355(49)	7.52
S(50)	50	18.4	96.946(28)	3.3132(23)	0.00180	3.5238(66)	0.092567(62)	7.45
S(60)	60	21.3	96.256(17)	3.7660(19)	0.00176	3.0467(85)	0.095402(45)	7.31
S(80)	80	26.5	95.309(23)	4.6972(21)	0.00177	2.3613(92)	0.098323(55)	7.33

^a The fitting residual error of the parameters A_m , A_r , τ_{mobile} , and τ_{rigid} are provided. $A_m + A_r = 1$ is restricted during the fitting procedures.

residual dipolar couplings is inversely proportional to M_C that indicates the molecular weight between two cross-linked points of silicone rubber chain.^[47] With appropriate distribution function (Gaussian or Gamma), the distribution of D_{res} can be obtained. D_{res} represents the structure of rubber matrix. Demonstrated with S(40) as the representative in Fig. 8(a), an original signal containing DQ signal I_{DQ} and a reference I_{ref} should translate into a build-up signal I_{nDQ} through:^[48]

$$I_{tail} = f \times \exp[-2\tau_{DQ}/T_2] \quad (11)$$

$$I_{MQ} = I_{ref} + I_{DQ} - I_{tail} \quad (12)$$

$$I_{nDQ} = \frac{I_{DQ}}{I_{MQ}} \quad (13)$$

where T_2 is the spin-spin relaxation time of the system, τ_{DQ} the double quantum (DQ) excitation time, I_{tail} the signal of monomer or free chain. I_{MQ} is used to normalize the DQ-filtered intensity and remove the influence of relaxations. An assumption that the residual couplings of series S(phr) and S_{FD} (phr) obey the Gaussian and Gamma distribution, respectively, is employed to put into the "Abragam-like" function:^[49]

$$I_{nDQ}(\tau_{DQ}, D_{res}) = 0.5 \left(1 - \exp \left\{ -(0.378 D_{res} \tau_{DQ})^{1.5} \right\} \cos [0.583 D_{res} \tau_{DQ}] \right) \quad (14)$$

Fig. 8(b) compares the DQ build-up curve of representative dry (S(40)) and swollen (S_{FD} (40)) samples. Intuitively, S(40) shows a clear maximum, while S_{FD} (40) shows a monotonic increase of the DQ intensity to the plateau value of 0.5, indicating a more homogeneous structure of the dry sample. Considering the different matrix network homogeneities between the dry and the swollen samples, two different fitting functions are used to get access of the D_{res} distribution. For the dry samples, relatively symmetrical rubber chains in matrix obey the Gaussian distribution. However, the asymmetry of chains caused by swelling makes fitting with the Gaussian

function no longer convergent. Thereby, the Gamma distribution is employed to fit the swollen samples.^[50] Fig. 8(c) presents the yielded residual dipole coupling $D_{res}/2\pi$ of the swollen (series S_{FD} (phr)) and dry (series S(phr)) samples as a function of Φ_{Si} . There is a critical threshold (Φ_{Si}^c) between 10 and 30 phr, and the significant difference appears with Φ_{Si} lower than 10 phr and higher than 30 phr. Moreover, the $D_{res}/2\pi$ values in each Φ_{Si} region are similar in series S(phr), as indicated by the red dash lines in Fig. 8(c). For series S(phr) samples with Φ_{Si} below and above Φ_{Si}^c , the $D_{res}/2\pi$ values are around 128 and 145 Hz, respectively. It suggests that the formation mechanisms of crosslinking density for the samples on the two sides of the critical threshold might be different. However, for series S_{FD} (phr), the $D_{res}/2\pi$ increases from 277 Hz to 345 Hz with increasing the Φ_{Si} from 30 phr to 80 phr. Interestingly, the $D_{res}/2\pi$ of S_{FD} (80) is significantly higher than that of other S_{FD} (phr) samples. The $D_{res}/2\pi$ values of series S_{FD} (phr) are constantly higher than that of series S(phr). Moreover, the distinct gap of $D_{res}/2\pi$ between two sides of Φ_{Si}^c in series S(phr) is declined in series S_{FD} (phr).

It should be noted that the residual dipole coupling includes the chemical crosslink and physical entanglements. Thus, σ/D_{res} is frequently utilized to represent the inhomogeneity of crosslinked network matrix, where σ is the standard deviation of Gaussian distribution.^[47] Fig. 8(d) shows that after surpassing Φ_{Si}^c , σ/D_{res} of series S(phr) increases monotonically from 0.25 to 0.45 with increasing the Φ_{Si} from 30 phr to 80 phr. For more intuitively describing the dipolar coupling distribution, a series of Gaussian distribution of S(30) to S(80) are graphically depicted in Fig. 8(e). The width of the measured dipolar coupling distribution curves broadens with increasing Φ_{Si} , suggesting that the asymmetry of polymer network is increased. In order to compare the Gaussian distribution of series S_{FD} (phr) and Gamma distribution of series

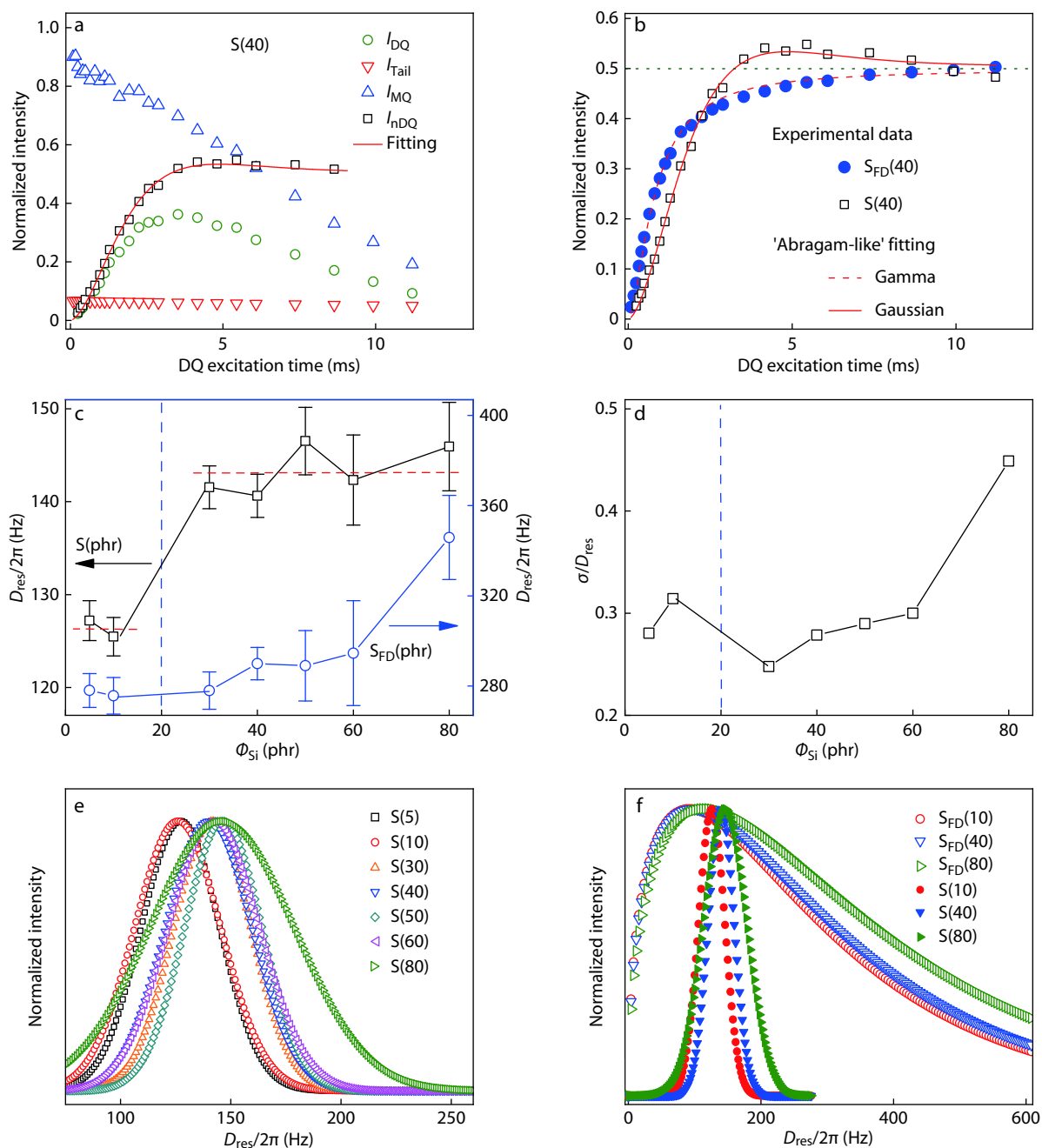


Fig. 8 (a) Demonstrated with S(40) as the representative, the normalized I_{DQ} , I_{MQ} , and I_{Tail} as a function of τ_{DQ} . The build-up I_{nDQ} fitted with 'Abragam-like' function. (b) The 'Abragam-like' fitting with Gaussian and Gamma distribution for dry (S(40)) and swollen ($S_{FD}(40)$) samples, respectively. (c) The $D_{res}/2\pi$ of swollen (series $S_{FD}(phr)$) and dry (series S(phr)) samples as a function of Φ_{Si} . (d) σ/D_{res} of series S(phr) as a function of Φ_{Si} . (e) The distribution of the filled silicone rubber network of series S(phr). (f) The comparison of $D_{res}/2\pi$ distributions for series S(phr) and $S_{FD}(phr)$.

S(phr), normalized D_{res} distribution curves with respect to their maximum amplitude are shown in Fig. 8(f). The network inhomogeneity of series $S_{FD}(phr)$ monotonically increases from 10 phr to 80 phr, indicated by the broadened D_{res} distribution. Obviously, swelling has a significant effect on the $D_{res}/2\pi$ distribution. Broadened distribution after swelling indicates that swelling could magnify inhomogeneous of the network.^[22]

DISCUSSION

Based on the CM-SANS, swelling kinetics, and low field ^1H -NMR results discussed above, several issues concerning different models of bound rubber related to filler fraction (Φ_{Si}) and filler structures can be clarified. A schematic illustration corresponding to these issues is drawn in Fig. 9. First of all, both the CM-SANS of series $S_{MP}(phr)$ and NMR data consistently

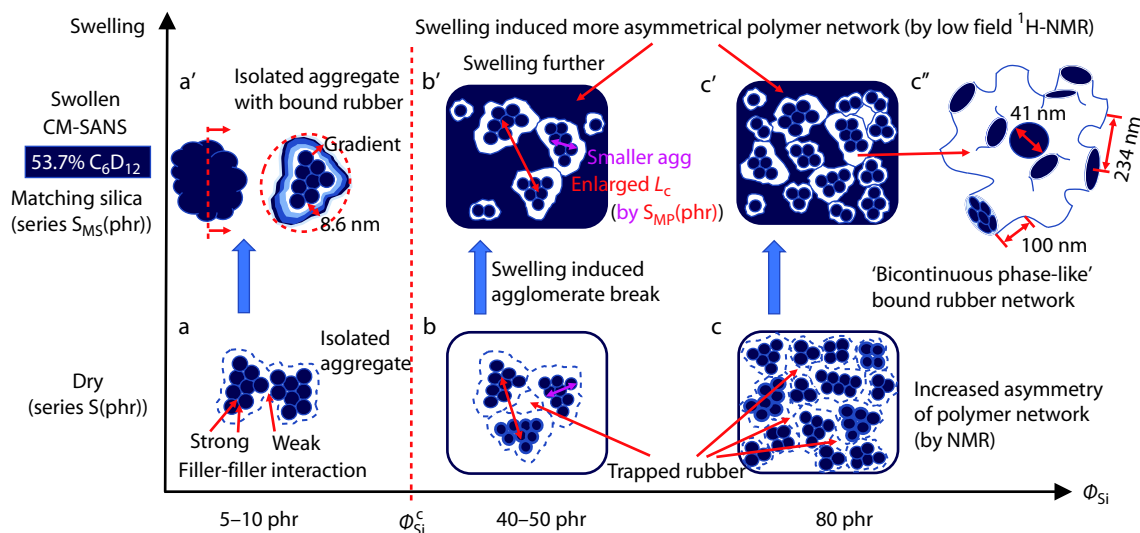


Fig. 9 Schematic illustration of the correlation between aggregates and bound rubber structures of (a, b, and c) dry samples and (a', b', c', and c'') swollen samples. The structure evolutions of samples with Φ_{Si} region below (a, a') and beyond Φ_{Si}^c (b, b', as well as c, c'). (c'') The three dimensional description of the bicontinuous phase-like bound rubber network found in $S_{MS}(80)$.

lead to a critical threshold Φ_{Si}^c between 10 and 30 phr, which is also in accordance with our previous work on $S(phr)$ ^[35] and the reported percolating threshold.^[51,52] When the Φ_{Si} is below Φ_{Si}^c , the correlation length cannot be detected in current observation scope, suggesting the isolated aggregates are dominant, as depicted in Fig. 9(a). With increasing the Φ_{Si} beyond Φ_{Si}^c , some portion of rubber is trapped among the aggregates formed agglomerate,^[9] as drawn in Fig. 9(b). The abnormal upturn of the half time of the swelling process ($t_{1/2}$) for samples from $S(40)$ to $S(60)$ in Fig. 1(b) suggests the existence of such trapped rubber. The swelling process leads to the break of the aggregated structures. Subsequently, the trapped rubber becomes 'free' again and restarts the swelling process for these rubber portions, which postpone the entire swelling process. The structural evolution during the swelling is demonstrated in the process from Fig. 9(b) to Fig. 9(b'). This can also be indicated by the expanded L_c of the swollen sample in Fig. 9(b') comparing with the dry samples in Fig. 9b (Fig. 3d). The significant different D_{res} extracted from NMR data in Fig. 8 suggests inherently different network textures exist in the rubber matrix below and above Φ_{Si}^c . Such diversity might originate from the different aggregate structures. Below the Φ_{Si}^c , the isolated aggregates can hardly form bound rubber network with any firm connection, as shown in Fig. 9(a'), while above the Φ_{Si}^c , the aggregates are more likely to be bounded with the percolating bound rubber network as the efficient bridges. Swelling process provides the driving force to influence connectivity of the filler network, thus, the gap of D_{res} between 10 and 30 phr is smeared out. The increased σ/D_{res} of $S(phr)$ and broadened D_{res} distribution of $S_{FD}(phr)$ in NMR data as a function of Φ_{Si} after surpassing Φ_{Si}^c (Fig. 8d) suggests the increased asymmetry of polymer network. As increasing the Φ_{Si} , more complicated filler network with various branching structures might induce more complicated and asymmetrical rubber matrix, which includes various occluded, trapped rubber. In addition, a monotonically rising $D_{res}/2\pi$ of series $S_{FD}(phr)$ after surpassing Φ_{Si}^c implies an likely increasing in the extent of

chain stretching, which contributes to the increasing of inhomogeneity.

Secondly, the Φ_{Si} -independent thickness around 8.6 nm found in the series $S_{MS}(phr)$ of CM-SANS data (Fig. 4) suggests that the formation of the bound rubber is determined by the inherent chemical and physic properties of the filler surface and the rubber chain. Interestingly, MSE-FID results (Table 2) also confirm such inherent character. It provides a Φ_{Si} -independent A_r/Φ_{Si}^v suggesting a normalized content of rigid component in the composite. Moreover, according to the model proposed by Saalwächter *et al.*,^[45,46] the thicknesses of bound rubber for $S(phr)$ yielded from NMR data are constant around 7.5 nm. On the other hand, the power-law around 4.2 in series $S_{MS}(phr)$ (Fig. 5) unveils that the bound rubber layer has exponential changed gradient density (Fig. 6), as schematically illustrated in Fig. 9(a'). Note that all the bound rubber layers are gradient and should be drawn as that of in Fig. 9(a'), however, for the sake of clarity, the gradient bound rubber in Figs. 9(b'), 9(c'), and 9(c'') are simplified to be the white regions. Rubber chains which are closest to the filler aggregates are the stiffest and are relatively hard to be swelled.^[9] The bound rubber gradient found within series $S_{MS}(phr)$ is in accordance with the descriptions of Papon *et al.*^[16] Current NMR data in Fig. 8 also suggest that the asymmetry of the rubber network is increased with increasing the Φ_{Si} after surpassing Φ_{Si}^c , which might come from the increased gradient structure and larger trapped rubber fraction. It should be kept in mind that 53.7% C_6D_{12} might not be the strict matching point of silica, since the swelling state of either polymer matrix or the bound rubber region is composed of both mixed solvent and polymer network. However, the experimental matching point (40%–60% $\Phi_{D-toluene}$) for silicone rubber in most q fractions is close to the calculated fractions of $\Phi_{D-toluene}=53.6\%$.^[34] It suggests that the bound rubber regions are the reliable main contributor for the SANS intensity of series $S_{MS}(phr)$. Thus, the present analysis and the corresponding conclusion are valid.

Thirdly, three character lengths of 41, 100, and 234 nm are found in $S_{MS}(80)$ (Fig. 4c). Combining with the exception power law of 2.4 of $S_{MS}(80)$, it suggests that a hierarchical structure of both the filler network and the polymer network is interpenetrated with each other. The bound rubber structure found in $S_{MS}(80)$ is likely a bicontinuous phase, as indicated in Fig. 9(c"). Three character lengths can be associated to the diameter and the length of the cylindrical tube filled with filler aggregates, and the inter-correlation length among the tubes, respectively. The absence of the peak set in the rest $S_{MS}(\text{phr})$ samples might be due to the relatively large aggregate sizes (Fig. 3c) and broad distribution, which are indicated by the intense intensity in the low- q region of series $S_{MS}(\text{phr})$, as well as the diversity of the Kratky representation of previous dry sample $S(\text{phr})$ ^[35] and current series $S_{MP}(\text{phr})$ (please see Fig. S1 in ESI). It suggests that the swelling process might somehow destroy the regularity of the filler network. Smaller aggregate size under swollen state in Fig. 3(c) confirms the above discussed swelling effect. It unveils that there are at least two kinds of filler-filler interactions in the aggregates. One is depending on the chemical interactions among the filler particle surfaces and physical interactions such as van der Waals forces and hydrogen bonding. Such filler-filler interaction is firm enough to sustain the swelling energy. The other is that aggregates just be adjacent to each other and weakly bonded. Such 'large' aggregates can be destroyed to 'smaller' portions by the outside field. However, the bound rubber network of $S(80)$ might be dense and strong enough to resist destruction by swelling, as stronger chain stretching is suggested by NMR data. Figs. 9(a)–9(c) to Figs. 9(a')–9(c') demonstrate the separation of such weakly contacted filler aggregates caused by swelling. The NMR results of series $S_{FD}(\text{phr})$ (Fig. 8f) also suggest that some topologically frozen inhomogeneities existing in series $S(\text{phr})$ would turn visible and amplified upon swelling.

Armed with the above information and previous work,^[35] the correlation between mechanical properties and hierarchical structures of the composites can be discussed. The swelling process could be treated as a good scenario to mimic the mechanical deformation on the samples. It is anticipated that swelling of filled rubbers is inhomogeneous due to the complicated distribution of rubber network. On the one hand, trapped rubber, the weak filler-filler interactions, and the outer layer of bound rubber can sustain the deformation and dissipate energy with the ability to recover, which ensures the performance of the composites. On the other hand, with the existence of strong filler-filler interactions, inner layer of the bound rubber shells remains throughout the aggregates, bridging of the bound rubber leads to a higher bound rubber fraction, and eventually an outer layer of occluded rubber is formed, contributing to the relatively high modulus. However, though $S_{MS}(80)$ presents the bicontinuous structure under swollen state, the aggregates are too close. Around the stiff filler network is still a relatively rigid rubber matrix dominated by the bound rubber layer and its gradient, causing the higher modulus while lower fracture strain. It means that the filler induced rubber chain dynamics modification at longer range is also sensitive to the mechanical behavior of the composites. The bicontinuous structure found in $S_{MS}(80)$ should also exist in the dry sample of $S(40)$ to $S(60)$,

which, however, is not clearly found in other $S_{MS}(\text{phr})$ samples. It might be caused by the destruction of bicontinuous structure during swelling process and by the high polydispersity of the structure. In fact, the polydispersity might also be the origin of the optimized flexibility compromising with the modulus.

In summary, we describe various bound rubber models associated with filler network structures with CM-SANS and low-field ^1H -NMR technique, with which the inherent reinforcing mechanisms are discussed. To optimize and balance the stiffness and flexibility of the composites is one of the most critical issues in the rubber community. In the past several decades, abundant studies indicate how sensitive the bound rubber is to various conditions, such as filler loading, additive, structure of aggregate, specific surface area, macromolecular parameters, processing conditions, etc. For this concern, aiming to use various bound rubber models to explain reinforcing mechanisms of the filled rubbers, the detailed description for bound rubber formation is of critical importance and needs continuous investigations.

CONCLUSIONS

Current work is aiming to investigate the correlation between bound rubber models and aggregate structures with various filler fractions Φ_{Si} in silicone rubber, combining contrast matching SANS, swelling kinetics, and low-field ^1H -NMR measurements. Three different C_6D_{12} fractions of 4.9%, 53.7%, and 100% were chosen to tune the neutron SLD of the solvent matrix. 4.9% ($S_{MP}(\text{phr})$) and 53.7% ($S_{MS}(\text{phr})$) are the matching points of PMVS and filler silica, respectively. The results support the variety of bound rubber models. (i) All the data consistently lead to a critical threshold Φ_{Si}^c between 10 and 30 phr. When the Φ_{Si} is below Φ_{Si}^c , the isolated aggregates are dominant. With increasing the Φ_{Si} to surpass Φ_{Si}^c , some portion of rubber is trapped among the aggregates formed agglomerate. The significantly different D_{res} extracted from NMR data suggests inherent different network textures exist in the rubber matrix below and above Φ_{Si}^c . The increased σ/D_{res} in NMR data as a function of Φ_{Si} after surpassing Φ_{Si}^c suggests the increased asymmetry of crosslink points. (ii) $S_{MS}(\text{phr})$ suggests a Φ_{Si} -independent bound rubber thickness around 8.6 nm. The NMR results also give an estimation of bound rubber thickness around 7.5 nm for all the $S(\text{phr})$ samples and provide a Φ_{Si} -independent A_r/Φ_{Si}^V , suggesting a normalized content of rigid component of the composite. Both data imply that the formation of the bound rubber is determined by the inherently chemical and physic properties of the filler surface and the rubber chain. Moreover, the power-law around 4.2 unveils that the bound rubber layer has exponentially changed gradient density. (iii) Three character lengths of 41, 100, and 234 nm are found in $S_{MS}(80)$, associated to diameter, length, and inter-correlation length of the tube, respectively. It suggests a hierarchical structure of both the filler network and the polymer network is interpenetrated. Accordingly, the inherent reinforcing mechanisms, as how the hierarchical structures, which include aggregates with both weak and strong filler-filler interactions, exponentially changed gradient bound rubber, trapped rubber, two kinds of filler-filler interactions, and asymmetrical rubber network, contribute harmonically to a

compromised strength and flexibility of the nanocomposites mechanical properties, are presented.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-019-2293-1>.

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