Structure of polymer solutions containing fumed silica

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Small angle neutron scattering is employed to estimate the interactions in complex multicomponent systems. The method is applied to describe a ternary system, poly(dimethyl siloxane) toluene with silica filler particles. Contrast variation by solvent deuteration is used to distinguish the three different partial structure factors of filled polymer samples, $S_{pp}(q)$, $S_{pf}(q)$, and $S_{ff}(q)$, where the subscripts p and f refer to polymer and filler. This procedure allows changes to be detected in the distribution of the polymer close to the solid surface. Independent dynamic light scattering measurements are used to validate the method. A comparison is made between the behavior of different filled poly(dimethyl siloxane) PDMS samples. It is found that the polymer distribution is perturbed in the vicinity of the solid surfaces. In the case of weak interactions, the solvent removes the polymer almost completely from the filler particles, while, when the interaction is strong, the surface remains covered.

I. INTRODUCTION

Finely divided filler particles have been used for many decades as reinforcing agents in elastomers and their effect on the resulting macroscopic elastic properties is well documented. It is also well known that the mechanical properties of filled systems (elastic modulus, tear strength, etc.) are sensitive to the surface treatment applied to the filler. Less well understood, however, is the effect of the polymer-filler interaction on the local distribution of polymer around filler on a submicroscopic length scale. Macroscopic measurements on filled gels are useful indicators of the reinforcing effect but are incapable of providing information on the strength of the local interactions that govern the underlying mechanism. Clearly, adsorption forces must play a central role in the adhesion of the polymer to the filler and these ultimately control the macroscopic mechanical behavior. Swelling measurements provide a simple and straightforward method of investigating the interactions in a filled polymer. As the network absorbs solvent molecules, elastic forces develop between polymer and filler, which affect the binding between the polymer molecules and the solid surface and ultimately leads to separation. These changes occur in a thin layer around the particles on a distance scale of the order of the size of a polymer molecule, i.e., 10–100 Å. Such length scales are ideally suited for small angle scattering investigations.

Recently we reported small angle neutron scattering (SANS) observations on poly(dimethyl siloxane) (PDMS) solutions and networks filled with fumed silica [1]. It was shown that this method was able to distinguish between the polymer distributions in the filled cross-linked and uncross-linked systems. A scheme was described for analyzing the scattering response of these ternary systems based on the inversion of the matrix of the partial structure factors. It was shown that the scattering contribution of the filler alone can be extracted from the combined signal of filler and polymer phase.

The aim of the present study is to obtain deeper insight into the interaction between polymer and filler particles by investigating the structural characteristics of the surface layer. To achieve this objective, two types of filler were used, with identical nominal surface area but having different surface treatments. Contrast variation with SANS is employed to obtain the partial structure factors of the various components. The present measurements were also intended to determine the surface coverage of the filler by the polymer and whether surface treatment has a detectable effect on this coverage. Such measurements, which, to our knowledge, have not previously been made, provide a direct method of estimating the interactions between the polymer chains and the filler particles in filled polymer systems.

II. EXPERIMENT

The polymer was a linear vinyl-terminated polydimethyl siloxane (Gelest). Two systems were investigated:

(1) a low molecular weight PDMS polymer ($M_\eta = 2 \times 10^4$), containing 25% w/w fumed silica [Degussa, Brunauer-Emmett-Teller (B.E.T.) surface area 300 $m^2 g^{-1}$] with octamethyl-tetrasiloxane grafted to its surface, designated $F0$.

(2) the same PDMS polymer as 1, but made with an identical filler that was additionally treated with hexamethyl disilazane to improve the interaction with the surrounding polymer ($F1$).

Both these samples were prepared by mechanically mixing the filler and the polymer melt in a ball mill under dry nitrogen at 70 °C for 3 hr. The resulting mixtures form thixotropic pastes that were swollen in toluene. The measurements

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reported here were performed on solutions with polymer volume fraction $\phi = 0.2$.

The samples were swollen in mixtures of hydrogenated toluene (Prolabo, analytical grade) and deuterated toluene (Acros) with deuterium content $>99\%$. The specimens for SANS were contained in a cell consisting of 1-mm thick quartz windows separated by a 1-mm spacer and sealed with a Viton O-ring.

The SANS experiments were done on the NG3 small angle instrument at NIST, Gaithersburg MD, using a wavelength of 8 Å. Two sample-detector distances were used, 3 m and 13.1 m. Counting times were between 20 min. and 1 hr. Calibrations were made with NIST standard samples [2]. Corrections for incoherent background were made with a method described elsewhere [3]. All measurements were carried out at room temperature (20°C).

Small angle x-ray scattering measurements were also made on the BM2 beamline at the European Synchrotron Radiation Facility at a wavelength of 1.59 Å. These measurements, using an indirectly illuminated CCD camera, explored only a limited part of the much wider q range available on this instrument, i.e., $6 \times 10^{-4} \leq q \leq 0.6$ Å^{-1}. The solutions were also measured by quasielastic light scattering to obtain the absolute intensity of the polymer-solvent concentration fluctuations. The light source used was a Spectra Physics 1161 argon-ion laser working at 488 nm, the measurements being made at 90° scattering angle. The correlation functions were constructed with an ALV E5000 correlator. Sample transmissions were measured with a Kontron Uvicon 810 spectrophotometer working at 488 nm.

III. THEORETICAL BACKGROUND

In binary gels, the scattering intensity can be described by the following expression [4,5]:

$$I(q) = (\rho_p - \rho_s)^2 \left(\frac{kT\phi^2}{M_{os}} \frac{1}{1+q^2\xi^2} + \frac{8\pi\Xi^3 \langle \delta\phi^2 \rangle}{(1+q^2\Xi^2)^2} \right), \quad (1)$$

where q is the scattering wave vector, $(\rho_p - \rho_s)^2$ the contrast factor between polymer and solvent, M_{os} the longitudinal osmotic modulus, and ξ and Ξ the correlation lengths describing the thermal and the elastic correlation lengths respectively. $\langle \delta\phi^2 \rangle$ is the mean square of the static concentration fluctuations. In the case of the present ternary systems composed of polymer, filler, and diluent, the situation is more complex. The scattering response is no longer described by a simple structure factor, but instead takes the form

$$I(q) = kT[(\rho_p - \rho_s)^2 S_{pp}(q) + (\rho_p - \rho_s)(\rho_f - \rho_s)S_{pf}(q)$$
$$+ (\rho_f - \rho_s)^2 S_{ff}(q)], \quad (2)$$

where ρ_f is the scattering length density of the filler. To solve for the three partial structure factors S_{pp}, S_{pf}, and S_{ff} that define the scattering components from the polymer, the filler, and of their mutual interface, $I(q)$ must be measured for at least three different values of the solvent scattering length ρ_s. This is achieved by swelling the sample in mix-
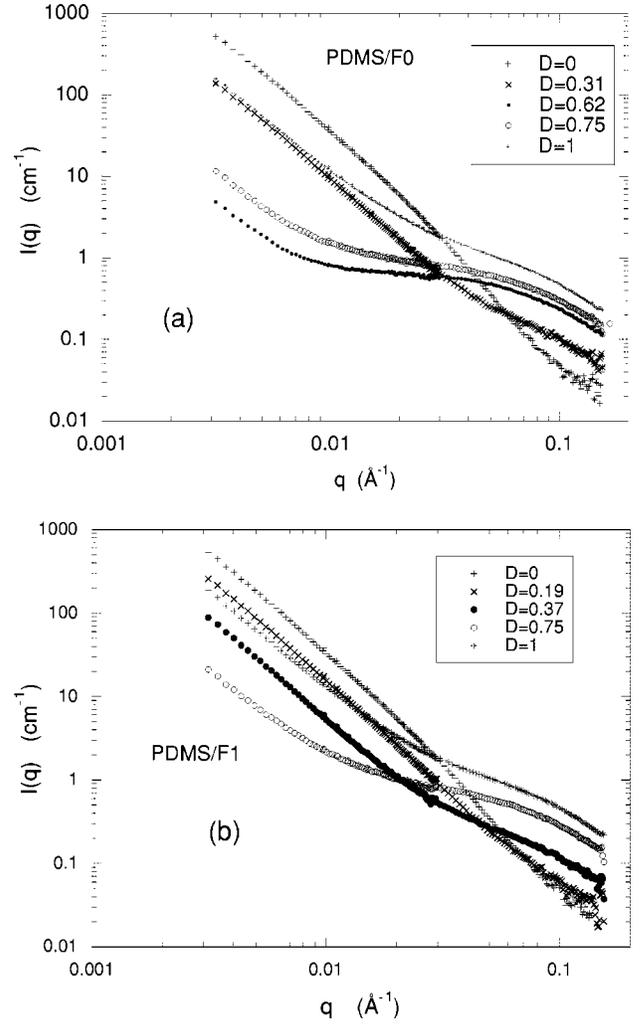

FIG. 1. SANS spectra of filled uncross-linked PDMS solution in toluene at five different values of D: (a) sample $F0$; (b) sample $F1$.

tures containing different proportions of deuterated solvent in order to vary the scattering power of the different components. The numerical values calculated from the literature for the scattering length densities are

$$\rho_p = 6.34 \times 10^8 \text{ cm}^{-2},$$

$$\rho_s = (0.944 + 4.738 \, D) \times 10^{10} \text{ cm}^{-2}, \quad (3)$$

$$\rho_f = 3.30 \times 10^{10} \text{ cm}^{-2},$$

where ρ_f was measured in reference [1] and D is the fraction of deuterated toluene in the solvent.

IV. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the normalized SANS spectra from the filled uncross-linked polymer solutions in toluene, at five different values of D. The structure factors $S_{ij}(q)$ are found by inserting the corresponding intensities $I(q)$ into Eq. (2) and inverting the matrix. Each of the resulting curves $S_{ij}(q)$, shown in Figs. 2(a) and 2(b), yields information on the distribution of matter in the sample. It can be seen that
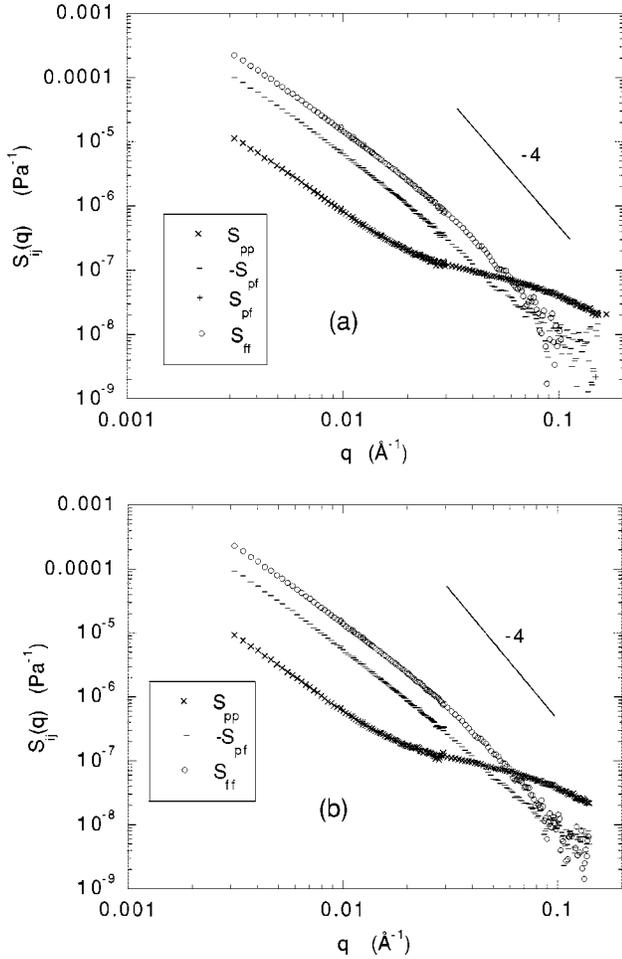
FIG. 2. Partial structure factors $S_{pp}(q)$, $S_{pf}(q)$, and $S_{ff}(q)$, calculated using Eq. (2) with the data from Fig. 1(a) and 1(b).

the general behavior of the responses of the two systems are very similar, with slight differences in the intensities of the different components.

The partial structure factors of the filler $S_{ff}(q)$ are also very similar. Figure 3 displays $S_{ff}(q)$ for sample $F1$, together with results from small angle x-ray and static light scattering. The latter measurements, made in the unswollen filled polymer, superimpose convincingly on the same curve. This agreement indicates that the distribution of the filler particles is not affected by the swelling of the polymer matrix. Also, the similarity between the structure factors of the silica in the free state and inside the polymer matrix shows that the mechanical mixing does not modify the size of the aggregates.

Several subregions of the curve in Fig. 3 display linear behavior, i.e., show apparent fractal character over a limited q range. In the intermediate q range, a slope of approximately -2.5 can be seen, while at higher q the limiting slope is -4, characteristic of Porod surface scattering [6]. From the latter region the surface area of the filler particles may be calculated on the basis of the expression [7]

$$\frac{\Sigma_f}{Vd} = \frac{\pi}{d} \frac{\lim_{q \to \infty} S_{ff}(q)q^4}{\int_0^\infty S_{ff}(q)q^2 dq}, \qquad (4)$$

where V is the scattering volume of the silica in the sample and d is its density. The numerical values found for this quantity are equal to 300 m^2/g for both samples, in good agreement with the B.E.T. values (see Table I). It is also noteworthy that the data of Fig. 3 can be described over the whole of the observed q range by the stretched exponential expression,

$$S_{ff}(q) = a \exp[-(qR_A)^n], \qquad (5)$$

where the exponent $n = 0.19$ and the characteristic length $R_A \approx 1$ cm. Equation (5), shown in Fig. 3 as a continuous line, yields a remarkable fit over the whole q range. At present, we can offer no satisfactory explanation for this observation.

The polymer-polymer scattering function $S_{pp}(q)$ obtained for both samples investigated here are also similar. The curve obtained for sample $F1$ is shown in Fig. 4. In this double logarithmic plot a quasilinear region is visible at small q, the general shape of the curve resembling that expected of a star polymer [8]. In the present case, however, because of the high concentration, the polymer chains emanating from the different stars overlap, and polymer system is therefore not a dilute but rather a semidilute solution. The data may therefore be described by an equation analogous to Eq. (1),

$$S_{pp}(q) = \frac{kT\phi^2}{M_{os}} \frac{1}{1 + q^2\xi^2} + \frac{A}{(1 + q^2\Xi^2)^{d/2}}, \qquad (6)$$

in which the exponent governing the q dependence of the second term is found to be $d = 3$ and A is an amplitude. The continuous line in Fig. 4 defines the least squares fit of Eq. (6) to the data, corresponding to the values

$$\xi = 13.6 \text{ Å},$$

where the value of the osmotic compressibility is

$$\phi^2/M_{os} = 1.07 \times 10^{-7} \text{ Pa}^{-1}. \qquad (7)$$

The first term of Eq. (6), corresponding to the thermodynamically driven concentration fluctuations, is displayed as a dashed line in this figure. The value found for Ξ is approximately 400 Å, i.e., the radius of the silica aggregates. For the sample $F0$ the fit to Eq. (6) is of similar quality, the numerical results differing by less than 10%.

The shape and intensity of the partial structure factors derived from Eq. (2) are sensitive to the assumptions adopted for the densities of the different components. Confirmation from independent observations is therefore necessary in order to validate these results. For this purpose, dynamic light scattering measurements [9] were made on solutions of the filled polymer in toluene at the same concentration as used for the SANS observations ($\phi = 0.2$). The resulting intensity correlation function, part of which is shown inset in Fig. 5, relaxes over many decades in time. The fastest relaxation, coming from the polymer-solvent gel mode, is heterodyned [10] by the strongly scattering silica clusters whose slow motion generates the long time relaxations visible in the figure. In the expanded view in Fig. 5, the contribution of the
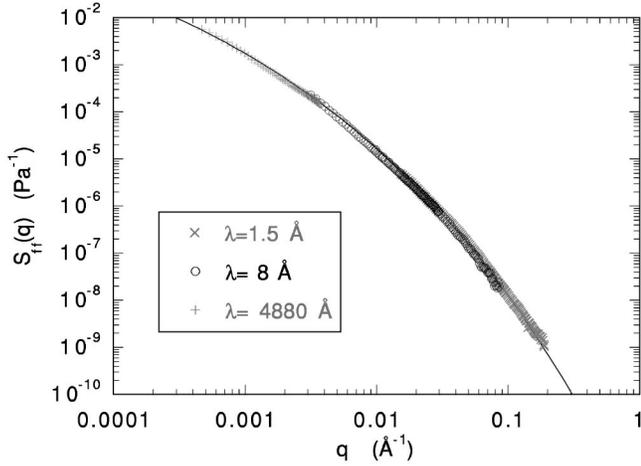
FIG. 3. Filler structure factor $S_{ff}(q)$ for sample $F1$ (○), together with measurements of the scattering intensity in the unswollen sample by static light scattering (+) and small angle x-ray scattering (×). The continuous line through the data is the stretched exponential expression (5) with $n=0.19$.
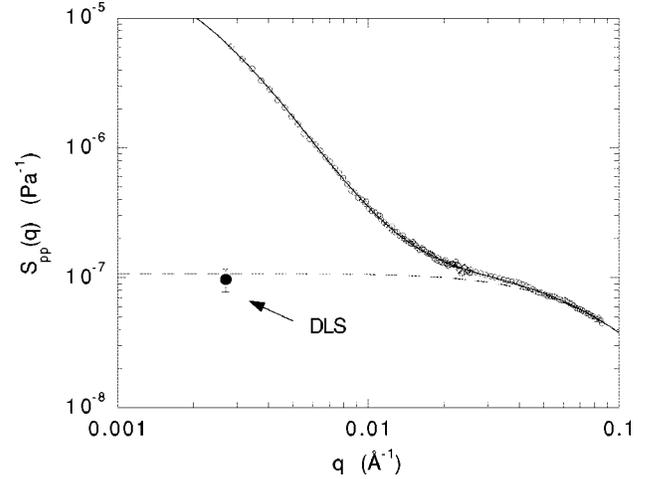

FIG. 4. Polymer structure factor $S_{pp}(q)$ for sample $F1$ (○) together with fit to Eq. (6) with $d=3$ (continuous line). Dashed line is first term in this fit and the filled symbol is the intensity of the thermodynamic fluctuations measured by dynamic light scattering.

polymer-solvent (gel) mode is visible in the initial (exponential) decay that relaxes towards the more slowly varying curve of the silica particles, visualized by the dashed line. The large difference between the relaxation time of the polymer concentration fluctuations (ca 7 μs) and the fastest translational mode of the silica particles (ca 20 ms) means that these two modes can be separated with a high degree of confidence. From the optical contrast factor $K = 4\pi^2 n^2 (dn/d\phi)^2 / \lambda^4$ and the ratio of the measured intensity of the fast mode to that of a toluene standard, the value of the osmotic susceptibility is found to be 0.98×10^{-7} Pa^{-1}. This datum point is displayed in Fig. 4 as a filled circle lying close to the horizontal plateau of the component of the neutron signal corresponding to the thermal fluctuations [first term in Eq. (6)]. The agreement between these two estimates of the intensity of the thermal fluctuations shows that the results obtained by the two independent techniques are consistent, thereby validating the procedure used to analyze the neutron scattering data.

The concepts employed above are now applied to compare the results of the polymer-filler interactions reported above with another uncross-linked PDMS system (sample II), containing a different filler (AE60, Degussa, ''hydrophobic'' filler at 9% w/w), the results of which were previously reported in [1]. Prior to the experiment, both systems were swollen in toluene to the same extent. In the latter system the

existence of a Porod region (i.e., with a slope -4) in S_{pp} at small values of q is observed (Fig. 6) that can be attributed to a smooth surface of polymer of approximate radius 500 Å. At low q values, significant differences appear between the responses of the two samples, notably a higher scattered intensity associated with the steeper slope for sample II.

From the scattering curves $S_{pp}(q)$ and $S_{ff}(q)$ the effective surface area of the filler covered by the polymer can be calculated using the corresponding Porod relations

$$\Sigma_p = \frac{kT}{2\pi} S_{pp}(q) q^4, \qquad (8)$$

in the region where the slope is equal to -4 and, for the filler particles,
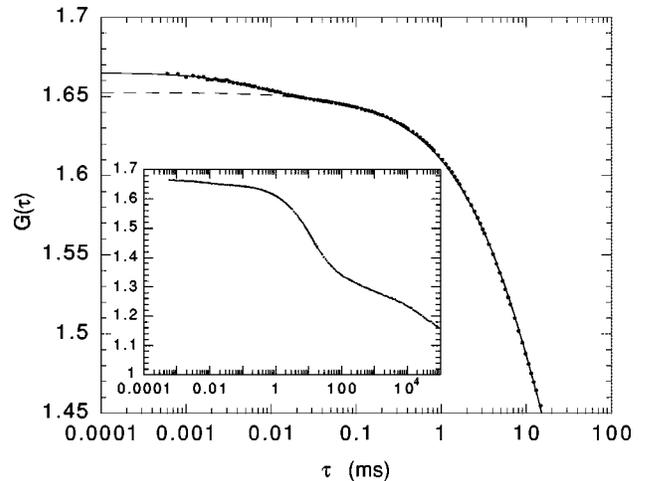

FIG. 5. Intensity correlation function $G(\tau)$ from sample $F1$, measured by dynamic light scattering at angle $\theta = 90°$ and incident wavelength $\lambda = 488$ nm. In the region $\tau \lesssim 50$ ms, the relaxation due to diffusion of the silica aggregates is described by a stretched exponential decay (dashed curve). The continuous curve describes the total relaxation, including that due to thermal concentration fluctuations between polymer and solvent.
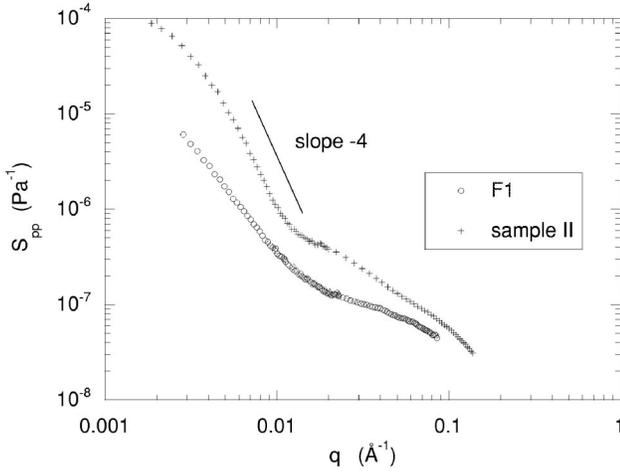
TABLE I. Specific surface area of silica filler measured by SANS, calculated from $\Sigma_f / V = [\pi \lim_{q\to\infty} S_{ff}(q) q^4] / [\int_0^\infty S_{ff}(q) q^2 dq]$.

Sample	$\Sigma_f / V d_{SiO_2}$[a] (m^2 g^{-1})	$\Sigma_{nom} / V d_{SiO_2}$[a] (m^2 g^{-1})
$F0$	300 ± 30	300
$F1$	300 ± 30	300

[a]$d_{SiO_2} = 2.089$ g cm^{-3}.

FIG. 6. Comparison between polymer structure factors $S_{pp}(q)$ in sample $F1$ ($\bigcirc$) and sample II ($+$). The region of Porod scattering in the latter case is indicated by a straight line with slope -4.

$$\Sigma_f = \frac{kT}{2\pi}\lim_q S_{ff}(q)q^4. \tag{9}$$

In case of poor surface adhesion of the polymer, it is expected, for entropic reasons, that the good solvent will significantly reduce the amount of polymer in contact with the surface and, furthermore, tend to expel polymer from confined spaces deep inside the filler aggregates. In that case a distinct polymer-solvent interface is generated at a certain distance removed from the solid surface, illustrated schematically in Fig. 7. For sample II (weak binding), the value of the surface coverage obtained from the spectra is found to be $\Sigma_p/\Sigma_f = 0.016$, implying that the polymer interface has little direct contact with the filler particles. The polymer is thus almost completely separated from the filler and forms a smooth polymer-solvent interface, which gives rise to the observed Porod scattering. This description is, of course, an oversimplification. In the region $q \approx 0.02$–0.05 Å^{-1} the response of sample II in Fig. 6 displays scattering in excess of that expected from Eq. (1). This indicates that concentration gradients are present in the polymer solution. Such a situation occurs when a small fraction of the polymer remains attached to the primary filler particles.

In the case of strong adhesion (e.g., attached chemically as in samples $F0$ and $F1$), the polymer molecules cannot be desorbed from the filler surface. For the latter samples, no free polymer surface can be identified in the low q region. This situation is expected for systems in which the surface of the solid particles remains covered by adsorbed polymer molecules. For such samples, however, it is difficult to evaluate Σ_p with confidence, since in the higher q region of $S_{pp}(q)$, it is increasingly difficult to discriminate the scattering contribution of the surfaces from that of the surrounding bulk polymer solution. Finally, it is noticeable in Fig. 6 that the scattering intensity S_{pp} from sample II significantly exceeds that of $F1$. This difference has to do with the higher polymer concentration inside the filler aggregates of $F1$ (due
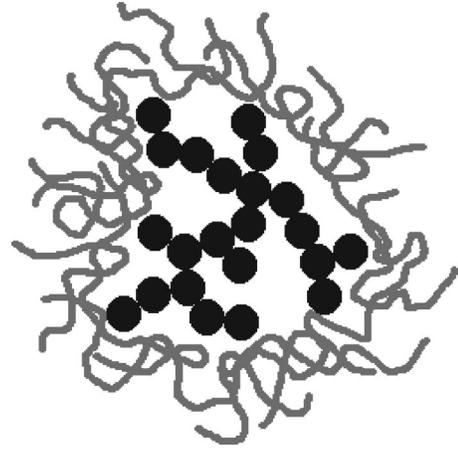

FIG. 7. Illustration of solvent-induced separation of polymer (continuous lines) at the outer limit of a filler aggregate. Dark circles represent primary silica particles.

to the improved coupling), and also with the high concentration of filler particles in $F1$, which causes the aggregates to interpenetrate strongly.

V. CONCLUSIONS

A method, based on small angle neutron scattering together with contrast variation, is used to characterize the polymer-filler interactions in poly(dimethyl siloxane) solutions and gels containing silica filler particles having different surface treatments. The neutron scattering response of the different components of this ternary system is separated in a consistent manner. This separation allows us to detect changes in the distribution of the polymer close to the solid surface. Independent dynamic light scattering measurements are used to validate the procedure. The method is applied to compare the behavior of filled PDMS samples in which the surface properties of the filler particles are different. In all cases it is found that the polymer distribution is perturbed in the vicinity of the solid surfaces. In the case of weak interactions, the solvent causes the polymer to desorb almost completely from the filler particles. In fillers treated with coupling agents, however, thorough penetration of the polymer into the filler structure is observed.

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