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Structure of Polymer Solutions and Gels Containing Fillers

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SUMMARY: Small angle neutron scattering (SANS) gives information on the structure of binary systems such as polymer solutions or swollen networks. By using mixtures of protonated and deuterated solvent the neutron scattering contrast can be varied, thus allowing ternary systems to be investigated. Here we describe SANS measurements in poly(dimethyl siloxane) (PDMS) solutions and gels containing fumed silica fillers with different surface treatments. Three different partial structure factors of the filled polymer samples can be distinguished, $S_{pp}(q)$, $S_{pf}(q)$ and $S_{ff}(q)$, where the subscripts p and f refer to polymer and filler. The structure factor of the polymer $S_{pp}(q)$ resembles that of star polymers. The distribution of the polymer in the network depends on the surface treatment.

Introduction

Understanding the structure of polymer networks has for long been a major challenge both for theoreticians and for experimentalists. Meanwhile, the outside world has added further complications to the task. Automobile tyre manufacturers (and others) routinely include finely divided filler particles, which yield a dramatic improvement in the properties of the elastomer. The macroscopic properties of the resulting networks are sensitive to the surface treatment applied to the filler. On a submicroscopic length scale, however, the effect of the polymer-filler interaction on the local distribution of polymer is not properly understood. Although these systems can be swollen in a diluent to reveal the inhomogeneities and local structure using traditional small angle X-ray or neutron scattering techniques (SAXS or SANS), the observed spectra consist of a sum of contributions from the polymer, the filler and their mutual interface. By varying the deuterium content of the diluent, however, SANS can distinguish between the different structure factors present in such ternary systems. Here we investigate poly(dimethyl siloxane) (PDMS) solutions and networks filled with fumed silica.1) Such measurements can be used to determine the internal surface area not only of the filler but also of the polymer in contact with it, as well as of the perturbations to the polymer

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concentration introduced by cross-linking. This technique is extended to systems containing fumed silica with different surface treatments.

Experimental

Four systems were investigated:

1) A poly(dimethyl siloxane) (PDMS) oil of viscosity 20 Pa s (Rhône-Poulenc Silicones), containing 9 wt% fumed silica (Degussa) with dimethylsilyl groups grafted to its surface. The BET specific surface area of this treated silica is 60 m^2g^{-1}. Prior to grafting, however, the nominal BET surface area of the untreated silica (Aerosil300) is stated to be 300 m^2g^{-1}. The resultant mixture forms a thixotropic paste that can be swollen in toluene. For the high polymer volume fractions ($\varphi = 0.2$) studied here, the resultant solutions are uniform and display no tendency to sediment.

2) The same as 2, but with in addition 4.3% w/w ethyl triacetoxysilane. This additive binds to the hydroxyl end-groups and establishes cross-links on exposure of the system to atmospheric moisture. After completion of the reaction, during which acetic acid is released, the residual weight fraction of this cross-linking additive falls to 1%.

3) Linear vinyl terminated PDMS of low molecular weight (Gelest), containing 25% w/w fumed silica (Degussa) with octamethyltetrasiloxane grafted to its surface.

4) The same PDMS polymer as 1, but in which the filler was additionally treated with hexamethyl disilazane to improve the interaction with surrounding polymer. Neither sample 3 nor 4 is cross-linked.

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 1mm spacer sealed with a Viton O-ring.

The SANS experiments were carried out at the ILL, Grenoble, using wavelengths of 12Å and 10 Å and at NIST, Gaithersburg, MD, USA using a wavelength of 8 Å. Counting times were between 20 minutes and 1 hour. Calibrations were made with water at 25°C using the NIST calibration procedure.$^{2)}$ Corrections for incoherent background were made with a method described elsewhere.$^{3)}$ All measurements were made at room temperature (20°C).

The density of the fumed silica used in these filled elastomers, measured by SANS contrast variation was previously found to be$^{1)}$

$$d_{\mathrm{SiO_2}} = 2.089 \text{ g cm}^{-3} \tag{1}$$

The measurements reported here were performed on solutions and gels with $\varphi = 0.2$.

Small angle X-ray scattering measurements were also made on the BM2 beamline[4)] at the European Synchrotron Radiation Facility at a wavelength of 1.59 Å. These measurements, using an indirectly illuminated CCD camera, explored a limited part of the much wider q-range available on this instrument ($6\ 10^{-4}$ Å$^{-1} \leq q \leq 0.6$ Å^{-1}). The solutions were, in addition, measured by quasi-elastic 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. Correlation functions were constructed with an ALV E5000 correlator (ALV Langen, Germany).

Results and Discussion

In the ternary systems of our present investigation, the SANS intensity $I(q)$ can be expressed in terms of three partial structure factors $S_{ij}(q)$, where the subscripts i and j refer to polymer (p) and filler (f). Thus

$$I(q) = kT\left[(\rho_p - \rho_s)^2 S_{pp}(q) + (\rho_p - \rho_s)(\rho_p - \rho_s)S_{pf}(q) + (\rho_p - \rho_s)^2 S_{ff}(q)\right] \qquad (2)$$

Here, ρ_p, ρ_f and ρ_s are the scattering length densities of the polymer, the filler and the solvent, respectively. The values calculated from the literature[5)] for these quantities are

$$\rho_p = 6.34\times10^{8}\ \text{cm}^{-2} \qquad (3a)$$

$$\rho_s = (0.944 + 4.738\ D)\times10^{10}\ \text{cm}^{-2} \qquad (3b)$$

$$\rho_f = 3.30\times10^{10}\ \text{cm}^{-2} \qquad (3c)$$

where ρ_f was found in ref.,[1)] and D is the fraction of deuterated toluene in the solvent.

Fig. 1 shows the normalized SANS spectra from a filled uncross-linked polymer solution in toluene (sample 3), at five different values of D. The total volume fraction of polymer + silica is φ=0.20. The structure factors $S_{ij}(q)$ are found by inserting the intensities $I(q)$ for each D into equation (2) and inverting the matrix. The resulting curves $S_{ij}(q)$ yield information on the distribution of matter in the sample. In a double logarithmic plot, the partial structure factor of the filler, $S_{ff}(q)$, shown in Fig. 2, displays three sub regions in which the behaviour appears to be linear, with slopes of approximately –1.8, –2.5, and –4, respectively. The first two of these sub regions can be interpreted in terms of fractal behaviour, while the last corresponds to surface scattering.[6)] In the same figure also are plotted the intensity from static light scattering and small angle X-ray scattering measurements from the same PDMS-filler system (without solvent). The consistency of the different data sets is excellent. To describe the data over a wide q range, a stretched exponential form is used:

$$S_{ff}(q) = a\exp[-(qR_A)^n] \qquad (4)$$

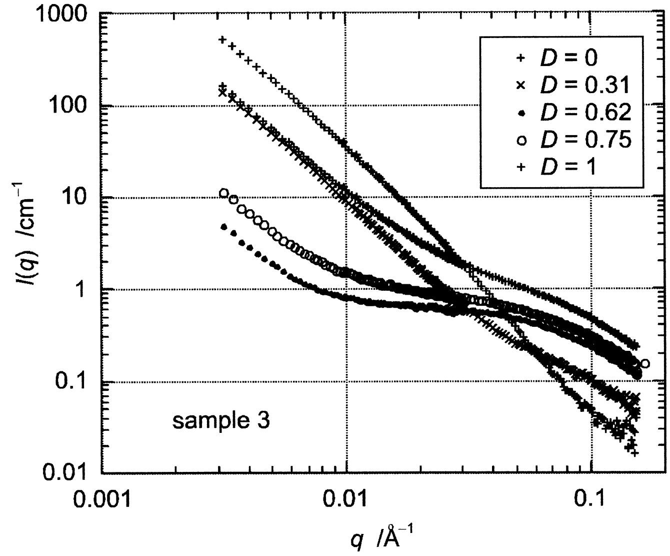

Fig. 1: SANS curves from sample 3 at five different values of D.

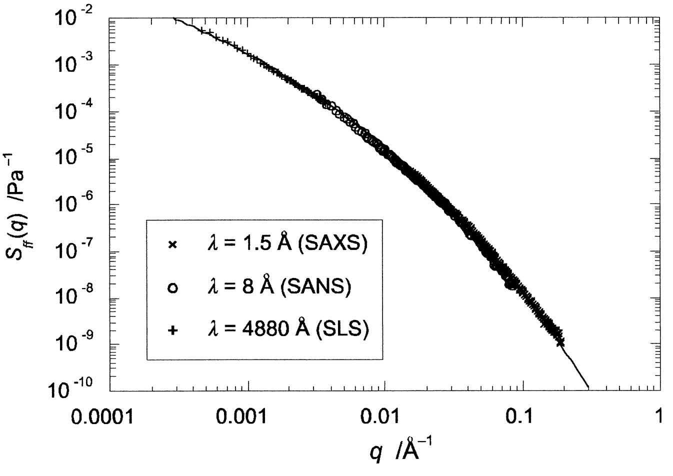

Fig. 2: Silica partial structure factor $S_{ff}(q)$ for sample 3 (o), together with $I(q)$ (for same sample in the absence of diluent) from static light scattering (+) and SAXS (x). Continuous curve: stretched exponential (equation 4).

where the exponent $n = 0.19$. Equation (4), shown in Fig. 2 as a continuous line, yields a remarkable fit over the whole q range. The exponent found here is different from that observed in ref.[1] for samples 1 and 2 (n=0.33). The explanation of this difference is not understood, but is necessarily related to the method of preparation of the silica filler. 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 primary aggregates. The results of $S_{ff}(q)$ for sample 3 are indistinguishable from those of sample 4.

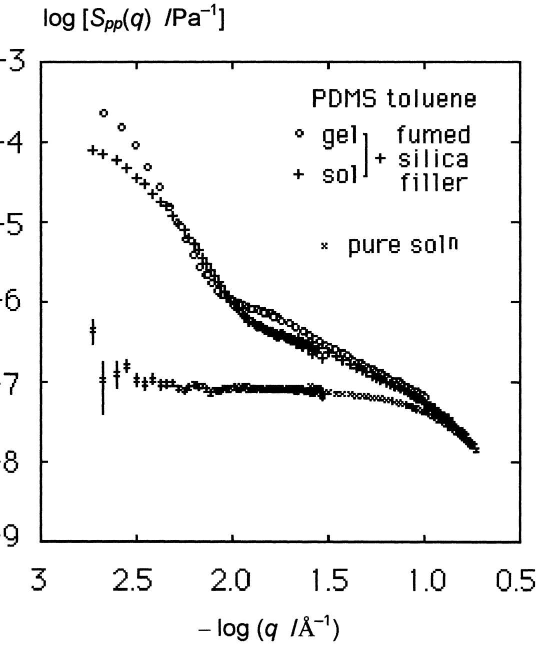

Fig. 3: Polymer-polymer partial structure factors $S_{pp}(q)$ in swollen PDMS gel containing silica (o) (sample 2), and in the corresponding uncross-linked solution (+) (sample 1). Also shown are the structure factors of a PDMS-toluene solution without filler (×). In the cross-linked system extra scattering due to frozen-in elastic constraints can be seen in the region $-2 > \log q > -1.5$

For samples 1 and 2 the polymer-polymer scattering functions $S_{pp}(q)$ are shown in Fig. 3, together with that of the unfilled solution. In this double logarithmic plot a slope of approximately −4 is visible in the small q region, corresponding to Porod scattering from a smooth surface.[6] From this region the surface area of the polymer in contact with the silica, Σ_P, can be evaluated[7]

$$\Sigma_p = \frac{1}{2\pi} q^4 S_{pp}(q) \tag{5}$$

The same procedure can be used to determine the corresponding surface area of the filler, which is found from the region of the spectrum $S_{ff}(q)$ varying in q^{-4}. The resulting ratio of these two sets of results yields for both sample 1 and 2

$$\Sigma_p/\Sigma_f \approx 0.02 \tag{6}$$

This finding means that, in the presence of the solvent, the loosely bound polymer is detached from the surface of the filler and forms a smooth shell around the aggregates without making intimate contact with the free surface area of the filler. The value of coverage found in this way is significantly lower than that deduced by indirect methods.[8)]

As with $S_{ff}(q)$, the curves $S_{pp}(q)$ for samples 3 and 4 are also identical, i.e. at the scale of spatial resolution defined by SANS, the polymer distribution in these two samples is indistinguishable. It differs markedly, however, from samples 1 and 2, in that the low q slope is close to -3 (Fig. 4). The general shape of the curve resembles that of star polymers.[9-11)] In the present case, however, because of the high concentration φ, the arms of different stars overlap; the polymer system is therefore not dilute but rather a semi-dilute solution. The data may therefore be described by the sum of two terms:

$$S(q) = \Delta\rho^2 \left[\frac{A}{(1+q^2\Xi^2)^{3/2}} + \frac{kT\varphi}{\partial\Pi/\partial\varphi} \frac{1}{1+q^2\xi^2} \right] \tag{7}$$

in which the second term corresponds to the usual Ornstein-Zernike expression for a polymer solution, ξ being the polymer-polymer correlation length and Π the osmotic pressure exerted by the solvent in the solution. The upper continuous line in Fig. 4 defines the least squares fit of equation 7 to the data, corresponding to the values $\xi = 13.6$Å

and

$$\varphi/(\partial\Pi/\partial\varphi) = 1.07\ 10^{-7}\ \text{Pa}^{-1} \tag{8}$$

In this fit, Ξ corresponds to the radius of the silica aggregates, its value being approximately 400 Å.

The shape and intensity of the partial structure factors derived from equation (2) are sensitive to the assumptions adopted for the densities of the different components. To validate the results, confirmation from independent observations is therefore necessary. For this purpose, quasi-elastic light scattering measurements[12)] were made on solutions of the filled polymer in toluene at the same concentration as used for the SANS observations ($\varphi = 0.2$). The resulting intensity correlation function, part of which is shown inset in Fig. 5, relaxes over many decades in time. The slower relaxations in this figure are due to diffusion of the silica aggregates in the uncross-linked solution (sedimentation effects are absent in these samples). The fastest relaxation, coming from the polymer-solvent gel mode,[13)] is heterodyned by the strongly scattering silica clusters. The contribution of the polymer-solvent (gel) mode is visible in Fig. 5 in the initial (exponential) decay towards the more slowly relaxing curve of the silica particles.

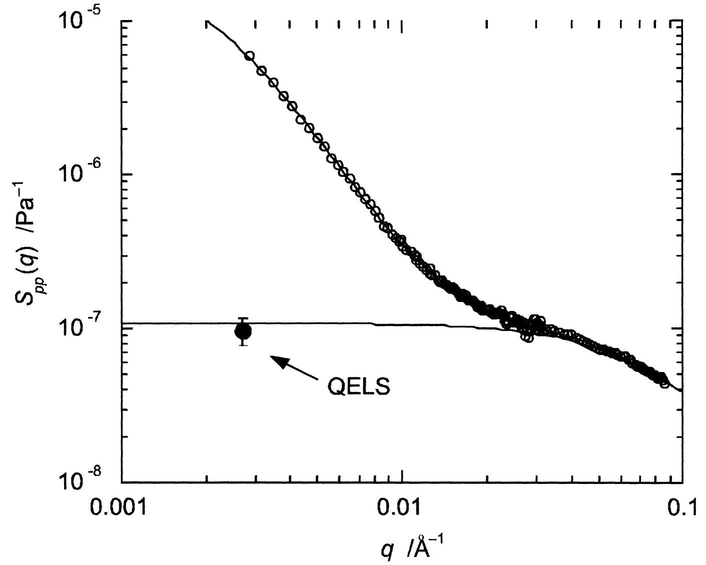

Fig. 4: Polymer-polymer partial structure factor $S_{pp}(q)$ in sample 4. The continuous line through the data points is the least squares fit to equation (7), the second (osmotic) term of which is the lower continuous curve. The point marked QELS is calculated from the intensity of the dynamic light scattering measurements in Fig. 5.

The large difference between the relaxation time of the polymer concentration fluctuations (ca. 7 μs) governing the osmotic pressure and the fastest translational mode of the silica particles (ca 20 ms) implies that these two modes can be separated with a high degree of confidence. From the ratio of the measured intensity of the fast mode to that of a toluene standard and a knowledge of the optical contrast factor $K=4\pi^2n^2(\mathrm{d}n/\mathrm{d}\varphi)^2/\lambda^4$ (λ is the wavelength of the incident light, n the refractive index) the value of the osmotic susceptibility is found to be 0.98 10^{-7} Pa^{-1}.[14,15] This result, shown in Fig. 4 as a single point, is in good agreement with the osmotic modulus calculated from the fit to equation (7).

For samples 1 and 2 the existence of a Porod region in S_{pp} at small values of q made it possible to associate an effective surface area occupied by the polymer around the silica aggregates. In samples 3 and 4 the observed slope in the low q region is approximately –3, indicating the presence of a polymer-rich region around the aggregate, but no specific surface area can be attributed to it. The absence of a sharp barrier implies that the polymer adheres to the surface of the aggregates, instead of generating a smooth plug at the outer surface. This result reveals that the different surface treatment of the filler in samples 3 and 4 is accompanied by a significant improvement of polymer adherence. For these samples, the only Porod behaviour observed is in the silica partial structure factor, $S_{ff}(q)$, from which the specific surface area Σ_f/V can be calculated, using the relation[7)]

$$\frac{\Sigma_f}{V}=\frac{\pi \operatorname{Lim}_{q\to\infty} q^4 S_{ff}(q)}{\int q^2 S_{ff}(q)\mathrm{d}q} \qquad (9)$$

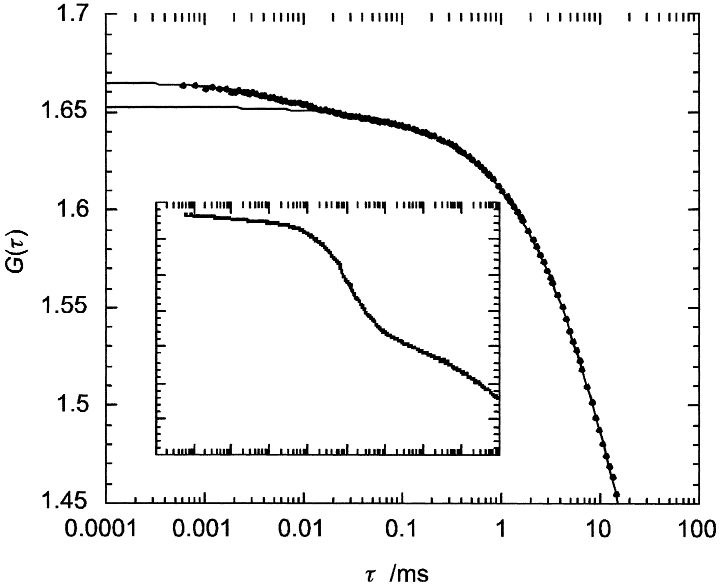

Fig. 5: Quasi-elastic light scattering correlation function of sample 4 in toluene. The fast relaxation (τ =7.0 μs) corresponds to polymer-solvent concentration fluctuations, while the slow relaxation describes the movement of the silica aggregates. The amplitude of the fast relaxation is used to calculate the osmotic modulus of the polymer solution.

Table 1: Specific surface area of silica filler measured by SANS, from equation (5) (taking d = 2.089 g cm^{-3}), compared with the nominal BET surface area.

Sample	$\frac{\Sigma_f}{Vd_{\mathrm{SiO_2}}}$ (m^2 g^{-1})	$\frac{\Sigma_{nom}}{Vd_{\mathrm{SiO_2}}}$ (BET) (m^2 g^{-1})
Dry Aerosil300	330±50	300
Sample 1(solution)	440±60	60
Sample 2 (gel)	270±40	60
Sample 3 (sol)	300±30	300
Sample 4 (sol)	300±30	300

where the denominator is the so-called scattering invariant, i.e., the second moment of the scattering curve. The values of Σ_f/V, listed in Table 1, are in excellent agreement with the nominal values obtained by BET measurements.

Finally, inspection of Fig. 3 reveals a notable difference between the cross-linked and the uncross-linked samples. The former displays marked extra scattering in the region $1/q \approx$ 50-100 Å, characteristic of the frozen-in concentration fluctuations that are associated with swollen cross-linked systems.16) To describe this feature, an extra term is required in equation (7).

Conclusions

Contrast variation measurements with SANS on PDMS melts filled with surface-treated fumed silica and swollen in toluene (samples 3 and 4) reveal that the polymer behaves at short distances like a normal semi-dilute solution, while close to the surface of the particles star-like character is observed. In samples 1 and 2 the surface treatment yields poorer contact between polymer and filler. In the latter group of samples, cross-linking produces static concentration fluctuations in a manner analogous to those in unfilled polymer gels.

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