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Silica filled elastomers: polymer chain and filler characterization in the undeformed state by a SANS–SAXS approach

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Abstract

The reinforcing phenomenon by blending soft elastomeric materials with rigid colloidal filler particles is, despite of its technological relevance, still poorly understood on the microscopic level although several macroscopic approaches have dealt with some of the mechanisms successfully. In order to contribute to bridge this gap, a study of a composite made up of a commercially silica-based hard phase and of a PI polymer matrix has been performed. The undeformed 'reference' state for such studies has been investigated by means of the small angle scattering technique on partially labeled samples. The single chain behaviour was isolated from neutron scattering although the condition of composition matching was not met, whereas the precipitated fractal filler structure was characterized by synchrotron X-ray scattering. The effective 3-component system has been successfully described through a combined approach of neutron and X-ray data and relationships dealing with 4-component structures have been presented. This work deals for the first time directly with the soft matrix in a reinforced 2-phase composite and is the basis for the treatment of anisotropic data in terms of both filler and chain dependence on uniaxial strain.

Keywords: Small angle scattering; Composites; Structure factors

1. Introduction

A main goal of today's research in polymers and composites in general is to obtain more insight in the complex reinforcing mechanisms which occur if polymers are blended with filler particles. The resulting modification of the mechanical properties is of crucial importance in the daily use as well as in the production of everyday life goods and especially for high performance rubber products as tires. Tire components are composites that benefit both from the elasticity of the rubbery component and from the stiffness of the reinforcing materials. The unambiguous characterization of both single constituents of this composite as well as their interactions is relevant for the further optimization of these materials in view of the increasing demands for better ultimate properties and higher economy. The full reinforcement is believed to be due to roughly 4 different contributions like (1) the filler–filler interaction, (2) the hydrodynamic effect, (3) the active filler–polymer coupling and (4) the basic chemical network of the polymer. A complete investigation of these contributions *separately* would involve an extensive modeling of parameters, however, and is practically impossible since the standard physical techniques are not selective to each single process. Many studies [1–4] on the reinforcing effect from fillers, most of which approach the problem from a mechanical point of view have been presented, investigating indirectly the microscopic properties through the study of the linear small amplitude viscoelastic responses of the composite as well as the large strain behavior.

Another family of works makes use of the scattering technique [5–7,25,26], as neutron and X-rays. Scattering techniques as such provide an important probe and to a good

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extent the reinforcement process can be decomposed into its constituents by the special interaction with the different probes. A detailed study of the chain structure in polymer networks under deformation can only be achieved by small angle neutron scattering (SANS) experiments on specifically labeled samples. A large scattering contrast is obtained by blending protonated chains with their deuterated counterpart. For filled networks the single chain behavior in the composite could be determined if contrast matching of the filler particles is reached. This condition is quite realistic in the case of a model system, whose composition is known and controllable. Then, by a suitable mixing of labeled and unlabeled chains the filler can be made invisible though its influence is inherently present [5,26]. As a more realistic system in Ref. [8], a study of a network with an in situ generated filler was presented recently. There, the single chain properties were determined using an approach designed mainly for the description of small angle scattering in polymer blends or concentrated solutions.

Here, we will try to tackle a very realistic system with a colloidal silica filler representative for fillers in actual industrial use. Such a filler has a fractal nature and should be treated at least as a 2-component system. As the second component the coating designed, e.g. for the improvement of the wettability of the polar SiO_2 surface of the filler which forms in this way a core-shell structure or even pores which are not accessible to the polymer matrix should be considered.

Consequently, to derive information from such a fairly realistic composite a 4-component system has to be considered: the protonated polymer, the deuterated polymer and a fractal filler which may include itself a 4th component. For this purpose a general scattering theory for such a system will be developed assuming thereby only incompressibility, a 2-phase-structure (filler/polymer phase) and no preferential interaction of one of the polymer components with the filler or its components. The main result will be the proof of additivity of filler or phase and chain scattering. This result determines the conditions for the matching of phase scattering and provides a rigorous basis for the extraction of chain scattering from the measured scattering intensities.

Using this approach, an important additional information about the filler structure is collected by means of SAXS measurements which are independent of the labeling degree of the soft matrix. This information will be used to check the theoretical results and to improve the accuracy of the determination of the contributions to the scattering intensity arising from the polymer.

In the past, this problem was considered mainly by 2 different approaches. In [15,9,16,17,26] methods typically used for multicomponent solutions or blend were applied. In this way, the typical 2-phase-structure of a filled network is neglected completely. A phase separated 3-component-system was considered in Ref. [25] applying several simplifications (e.g. the assumption of identical polymer chains) and approximations. Latter system is covered by our considerations and the main results agree for the limiting case, too. For the consideration of the consequences of the incompressibility assumption through all derivations in this paper, the discussion of compressibility contributions in Ref. [25] may be useful.

This first approach to the problem applies to the isotropic reference state so that the properties of both filler as also the polymer can be cross-checked with literature. In the follow-up paper, the extraction of the polymer and filler intensities will be applied to deformed samples, from which the determination of the behaviour under deformation for both phases is now accessible independently. Whereas the emphasis here is on the methodical aspects, the forthcoming publication will deal with the reinforcement of these samples on different length scales.

2. Experimental

Protonated and deuterated polyisoprene homopolymers were synthesized through the technique of anionic polymerization. The initiator was *sec*-butylithium and the reaction is carried out in *n*-hexane under high vacuum. This guarantees high monodispersity in the final product and reduces coupling reactions of the living anion due to the presence of impurities in the reactor. The polymerization process [10] leads primarily to a 4,1 addition [11] and yields a microstructure of 78% of the *cis*-isomer and of 14% of the *trans*-isomer. The remaining 8% corresponds to 4,3 addition. The final products had virtually identical molecular weights as obtained from LALS and osmometry (values for D-PI converted to the protonated equivalent: $M_w = 196,000$, $P = 1.019$, H-PI : $M_w = 206,000$, $P = 1.020$).

The activated fillers Coupsil 6105 and Coupsil 6109 used in this study as such belong to a series of experimental products from Degussa AG and were kindly provided. Their basic structure consists of a spherical silica core (Ultrasil VN2, Degussa). The size distribution of the core, measured with TEM, corresponds to a Schultz distribution

$$f(r) = A\left(\frac{z_s+1}{\langle r\rangle}\right)^{z_s+1} r^{z_s}\,\frac{e^{-(z_s+1)r/\langle r\rangle}}{\Gamma(z_s+1)} \qquad (1)$$

with prefactor $A = (2976 \pm 5)$, polydispersity parameter $z_s = (16.1 \pm 0.1)$ and average radius $\langle r\rangle = (148 \pm 1)$ Å. Determination of the specific surface (Degussa) gives a value of $S_{spe} = 120\ m^2/g$ corresponding to a radius $r = 3/(S_{spe}\rho) = 125$ Å, if the density $\rho = 2.0\ g/cm^3$ is assumed.

The core of the primary particles is chemically modified and grafted to yield in a first approximation a smeared layer which is constituted of a bifunctional organosilane (SI69, TESPT, $C_{18}H_{42}Si_2S_4$). The structure of the shell is manyfold and contains loops as well as loose chain ends [12]. Coupsil 6105 and 6109 contain, respectively, 5 and 9% v/v SI69 unities. The grafting reaction introduces an intrinsic uncertainty with respect to the expected scattering behaviour. The presence of residual water, estimated by Degussa to be up to 9% after drying as well as of chemicals from the precipitation process, may lower the scattering length density of the theoretical shell by an unknown factor and hampers the exact matching of the intrinsic 4-component system. This lack of information affects the a priori determination of the actual values of the scattering length densities of the filler components. Therefore, as a good approximation the scattering length of the layer will be obtained using tabulated values of the specific volume for the SI69 groups [13] and the corresponding scattering lengths [14]. Other impurities are neglected.

Eight network samples, differing in labeling degree and filler volume fraction, were prepared and their compositions are listed in Table 1. The polymers as well as the crosslinker dicumylperoxide (DCP) were mixed in solution (THF), the silica was dispersed in them and the viscous solution was casted in a teflon mould and the solvent evaporated. From the uncertainty on the density and weighing accuracy filler degrees are determined to be ≈ 1%. Permanent networks were obtained by chemical crosslinking at 140 °C under vacuum and under slight mechanical pressure ($P \approx 30$ bar) for 1.5 h. The resulting mesh sizes M_C, determined from swelling in cyclohexane and assuming that the silica particles are not modified by the presence of the solvent and do not influence the swelling of the matrix, are listed in Table 1. The gel fractions are 99% and higher. The experimental spread in M_C may be due to additional S-diene crosslinking with the filler surface and inevitably varying stoichiometric DCP concentrations. The uncertainty on M_C is estimated as 10% in view of the assumptions made in the swelling of filled rubbers. The thickness was about 1 mm to avoid multiple scattering.

SANS experiments were performed on SAND (ANL, Chicago), SANS-1 (PSI, Villigen) and KWS1 (FZJ, Jülich). The first instrument is a TOF diffractometer with a wavelength range spanning from 1 to 14 Å, while SANS-1 uses a single wave length of 7 Å with $\Delta\lambda/\lambda = 0.1$. Both are located at a spallation source. A steady reactor was the neutron source for the KWS1 spectrometer, which uses $\lambda = 7$ Å with $\Delta\lambda/\lambda = 0.2$. Detector distances varied typically from 2 to 20 m. Corresponding scattering vectors q between 2×10^{-3} and 2×10^{-1} Å^{-1} were obtained. All data were collected two-dimensionally and absolutely calibrated through a lupolene of water secondary standard after appropriate channelwise correction for background scattering and sensitivity and agreed except for small absolute intensity differences. The macroscopic differential cross section $\mathrm{d}\Sigma/\mathrm{d}\Omega$, often in the text abbreviated by intensity is defined as $\mathrm{d}\Sigma/\mathrm{d}\Omega = (1/V_s)\mathrm{d}\sigma/\mathrm{d}\Omega$ with V_s the sample scattering volume to yield the cm^{-1} unit. SAXS data were obtained from the high brilliance ID2 spectrometer at the ESRF, Grenoble. The scattering vector range accessible by the pinhole SAXS camera was $0.005 \le q \le 1$ Å^{-1} and therefore overlaps with the available SANS data. The detector type used was an image intensified CCD camera. The necessary corrections for CCD dark current and the offset of the analogue to digital converter, spatial distortions, the small spatial inhomogeneities in the quantum efficiency were applied to convert the raw intensities to approximated absolute values.

Table 1
Composition of the samples. ϕ_d is the fraction of labeled polymer in the rubbery phase and ϕ the total volume fraction of filler 6105 (^{v} filler was 6109). The accuracy on ϕ and M_C are discussed in Section 2. V-samples have been investigated on SANS-1, C-samples mainly on SAND

s.n	ϕ_d	ϕ_h	ϕ	M_C
2C99	0.00	1.00	0.02	8500
3C99	0.00	1.00	0.08	5000
4C99	0.00	1.00	0.15	3900
2V99	0.40	0.60	0.08^{v}	11,400
5C99	0.40	0.60	0.08	10,300
7C99	0.34	0.66	0.08	10,000
3V99	0.40	0.60	0.15	6100
6C99	0.40	0.60	0.15	8200

3. Scattering in multicomponent systems

Polymer–filler systems are complicated and structured multicomponent systems. Extracting the information of interest from scattering results therefore demands sophisticated labelling techniques as well as a suitable theoretical treatment.

As already discussed in Section 1, due to a possible core-shell or porous structure of the filler particles, our system has to be considered most generally as a 4-component problem. The total differential cross section for such a system, characterized by constant scattering lengths of the scatterers can be expressed by 4 diagonal (intra-component) and 6 off-diagonal (inter-component) partial structure factors as

$$\begin{aligned}\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} &= b_1^2 S_{11} + b_2^2 S_{22} + b_3^2 S_{33} + b_4^2 S_{44} + 2b_1 b_2 S_{12} \\ &\quad + 2b_1 b_3 S_{13} + 2b_1 b_4 S_{14} + 2b_2 b_3 S_{23} + 2b_2 b_4 S_{24} \\ &\quad + 2b_3 b_4 S_{34} \qquad (2)\end{aligned}$$

The q-dependence was omitted for clarity. If the system is treated incompressible, the number of necessary partial structure factors can be reduced using the sum rules

$$\sum_j S_{ij} = 0 \qquad (3)$$

The scattering properties for well-known 2- and 3-components systems can be conveniently expressed in terms of intra-component structure factors only. For a polymer–filler system the 2-component system, with $S_{11} = S_{ff}$, $S_{33} = S_{pp}$, $S_{13} = S_{fp}$,

$S_{22} = S_{44} = S_{12} = S_{23} = S_{24} = S_{14} = S_{34} = 0$, $b_1 = b_f$, $b_3 = b_p$ in Eq. (2) simply results in

$$S_{ff} = S_{pp} = -S_{fp} \tag{4}$$

and

$$\frac{d\sigma}{d\Omega} = (b_f - b_p)^2 S_{ff} \tag{5}$$

Analogously for a 3-component system,

$$\frac{d\sigma}{d\Omega} = (b_1 - b_2)(b_1 - b_3)S_{11} + (b_2 - b_3)(b_2 - b_1)S_{22} + (b_3 - b_1)(b_3 - b_2)S_{33} \tag{6}$$

is obtained from which trivial matching conditions can be seen.

For 4-component systems such a presentation is not possible but the contributions to Eq. (2) from one component can be eliminated easily. This may be a suitable approach if in some way one component is especially distinguished, which is not the case in this work, however. A more suitable treatment is possible assuming that our 4-component system forms a 2-phase system with 2 incompressible phases formed by 2 components, respectively. These 2 components are the filler and a shell or pores for the filler phase (i.e. 1,2) and the 2 polymer components for the polymer phase (i.e. 3,4). The partial structure factors of the phases fulfill the relationship (4) and the intra-phase inter-component partial structure factors can be expressed by S_{pp} and the intra-component structure factors alone as

$$S_{12} = (S_{pp} - S_{11} - S_{22})/2 \tag{7}$$

$$S_{34} = (S_{pp} - S_{33} - S_{44})/2 \tag{8}$$

If there is no preferential interaction of one of the polymer component with the filler components the relationship

$$S_{13} = \frac{\Phi_3}{\Phi_4} S_{14} \tag{9}$$

results naturally. For the polymer bulk phase the RPA chain–chain correlations exist which yield for the diagonal polymer structure factors

$$S_{33} = \Phi_3^2 S_{pp} + \Phi_p S_{\mathrm{RPA}} \tag{10}$$

$$S_{44} = \Phi_4^2 S_{pp} + \Phi_p S_{\mathrm{RPA}} \tag{11}$$

Using relations (7), (8), (9), (10) and (11) and as well as the incompressibility conditions (3) one obtains

$$\frac{d\sigma}{d\Omega} = (b_1^2 - b_1 b_2 + (b_2 - b_1)b_{\mathrm{p,av}})S_{11} + (b_2^2 - b_1 b_2 + (b_1 - b_2)b_{\mathrm{p,av}})S_{22} + (b_1 b_2 + b_{\mathrm{p,av}}(b_{\mathrm{p,av}} - b_1 - b_2))S_{pp} + \Phi_{\mathrm{p}}(b_3 - b_4)^2 S_{\mathrm{RPA}} \tag{12}$$

with average scattering length of the polymer phase

$$b_{\mathrm{p,av}} = \Phi_3 b_3 + \Phi_4 b_4 \tag{13}$$

Eq. (12) represents the differential cross section in the general case of a polymer–filler system with a 2-component filler. Such a system would be characterized by 3 partial structure factors of the polymer–filler phase and the RPA structure factor of the chains.

Eq. (12) may be further simplified in the assumption that both filler components are randomly or homogeneously distributed over the filler phase. Then with

$$S_{11} = \Phi_1^2 S_{pp}, \qquad S_{22} = (1 - \Phi_1)^2 S_{pp} \tag{14}$$

the differential cross section results as

$$\begin{aligned}\frac{d\sigma}{d\Omega} &= (b_1\Phi_1 + b_2(1 - \Phi_1) - b_{\mathrm{p,av}})^2 S_{pp} + \Phi_p(b_3 - b_4)^2 S_{\mathrm{RPA}} \\ &= (b_{\mathrm{f,av}} - b_{\mathrm{p,av}})^2 S_{pp} + \Phi_p(b_3 - b_4)^2 S_{\mathrm{RPA}}\end{aligned} \tag{15}$$

From Eqs. (12) and (15) it follows immediately that in the case of the effective 3 component system a matching point

$$\begin{aligned}\Phi_3 &= (b_1\Phi_1 + b_2)(1 - \Phi_1) - b_4)/(b_3 - b_4) \\ &= (b_{\mathrm{f,av}} - b_4)/(b_3 - b_4)\end{aligned} \tag{16}$$

exists, whereas for the full 4-component system 2 partial matching points with vanishing prefactors for S_{11} and S_{pp} or S_{22} and S_{pp}, respectively, occur at the volume fractions

$$\Phi_{3,1p} = (b_1 - b_4)/(b_3 - b_4) \tag{17}$$

$$\Phi_{3,2p} = (b_2 - b_4)/(b_3 - b_4)$$

Both cannot be fulfilled at the same time which prevents full matching out of all filler contributions. Eqs. (12) and (15) provide a rigorous theoretical basis for the investigation of any polymer filler system. In both cases, however, the additivity of phase and chain scattering is prominent. Consequently, the chain scattering contribution can in principle be determined for matching as well as for off-matching conditions if the contributions of phase scattering are derived precisely enough from the experimental data. This problem will be discussed below in detail.

First of all, a clear identification of the phase scattering is necessary. In this way, using the shown additivity property a rigorous determination of the chain scattering is possible even for systems which are far off the matching condition.

4. Filler characterization

The investigation and characterization of the phase scattering will use SANS and SAXS data from the same sample in 2 different ways. Considering that in the q-range of our investigations the X-ray form-factors of the monomeric groups of our polymers can be taken constant, the SAXS contrast is characterized by scattering length densities alone as is the SANS contrast. Investigating pure protonated samples with $b_3 = b_4$ and therewith vanishing chain scattering contrast for SAXS and SANS allows the phase scattering to be quantified according to Eqs. (12) or (15), respectively. A decision whether the 2-component case with one structure factor in Eq. (15) or the 3-component case with 3 structure factors according to Eq. (12) applies, then becomes possible if we assume that the relationships between the 3 scattering lengths b_1, b_2 and $b_{\mathrm{p,av}}$ in Eq. (12) are different for neutrons and X-rays. For the real 2-component filler different q-dependencies for SAXS and SANS should be expected whereas an undistinguishable scattering should result for both probes from an averaged filler in Eq. (15).

The experimentally shown congruence of SAXS and SANS data as shown in Fig. 1 therefore allows a considerable simplification for the description of the filler scattering. From this observation and with Eq. (15), we conclude that for a labeled sample the SANS method yields the sum of phase and chain scattering whereas SAXS is limited to the phase scattering only. Consequently, the chain scattering can be determined unambiguously from 2 measurements on the same (labeled) sample if the structure factor S_{ff} or S_{pp} from SAXS is substituted in Eq. (15) as it proved to be identical (see below). Therefore, all samples have also been measured with synchrotron radiation and analyzed with respect to their q-dependence, irrespective of their deuterium labeling.

A suitable model which is used to describe S_{ff} or equivalently S_{pp} for such a filler is the empirical model of Beaucage [18–21]. The main assumptions of this model are the additivity of cluster and particle scattering and also an additive combination of a Guinier law and a structurally limited power law as characterization of both levels. The parameters of this model are the average radius of gyration $R_{\mathrm{g,p}}$ and fractal surface dimension d_{p} of the primary particles on the one hand, and the radius of gyration $R_{\mathrm{g,cl}}$ and a mass fractal dimension d_{cl} of clusters formed in average by z primary particles on the other hand. The structure factor of the Beaucage-model then reads

$$\begin{aligned} &S_{ff}(q, R_{\mathrm{g,p}}, d_{\mathrm{p}}, R_{\mathrm{g,cl}}, d_{\mathrm{cl}}) \\ &\quad \simeq H_1 \exp\left(\frac{-q^2, R^2_{\mathrm{g,cl}}}{3}\right) + H_2 \exp\left(\frac{-q^2 R^2_{\mathrm{g,p}}}{3}\right) \\ &\quad \times \left[\frac{(erf(qR_{\mathrm{g,cl}}/\sqrt{6}))^3}{R_{\mathrm{g,cl}} q}\right]^{d_{\mathrm{cl}}} + H_3 \exp\left(\frac{-q^2 R^2_{\mathrm{g,p}}}{3}\right) \\ &\quad + H_4 \left[\frac{(erf(qR_{\mathrm{g,p}}/\sqrt{6}))^3}{R_{\mathrm{g,p}} q}\right]^{d_{\mathrm{p}}} \end{aligned} \qquad (18)$$

In Eq. (18) the factor $\exp(-q^2 R^2_{\mathrm{g,p}}/3)$ considers the high-q cutoff of the cluster scattering on the scale of the particle dimensions. Details of the prefactors H_i are here not of interest, except for H_1. The relationship $H_1 = zH_3$ serves for the estimation of the average number of particles in a cluster, i.e. the aggregation number. For the discussion of the effective scattering contrast of the filler only the estimation $H_1 \simeq S_{ff}(0)$ is of importance. The fitted curves of SANS for 3 fully protonated filled samples with Eq. (18) are shown in Fig. 2. These intensities were fully calibrated and normalized to unit volume. From the prefactors, e.g. scattering lengths can be extracted. With the earlier definition of the macroscopic differential cross section $\mathrm{d}\Sigma/\mathrm{d}\Omega$, H_1 reduces to $\phi_f z V_{\mathrm{p}} (\Delta\rho)^2/v_0^2$. V_{p} is the primary particle volume and v_0 the monomeric volume of a polyisoprene unit. $\Delta\rho$ is the scattering length density difference between matrix and silica. The agreement of the fit with the experimental data is agreeable. It confirms the simple 2-component, averaged filler phase assumption. The Beaucage parameters for all investigated samples, specifying the nature and architecture of the filler are summarized in Table 2. Two distinct domains characterized by the slope $d_{\mathrm{cl}} = 2.5$ and $d_{\mathrm{p}} = 3.28$ are consistent with the 2-level hierarchy. The experimental radius $R_{\mathrm{p}} = 124$ Å of SANS compares reasonable well with TEM results (148 Å) and USAXS

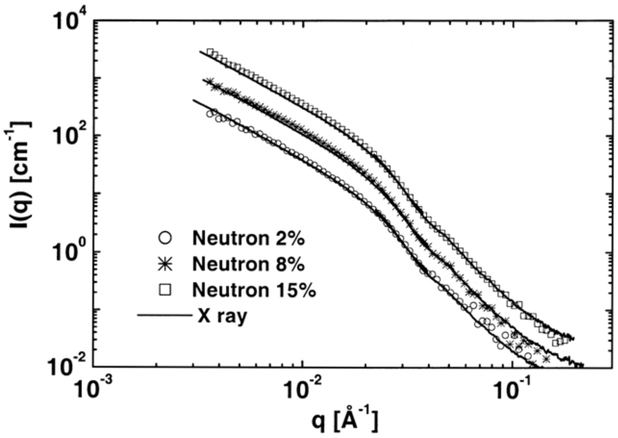

Fig. 1. Comparison of the X-ray data with the neutron data for protonated samples (2C99, 3C99 and 4C99). The agreement is very good and excludes measurable contributions from internal density fluctuations inside the particle, i.e. a shell.

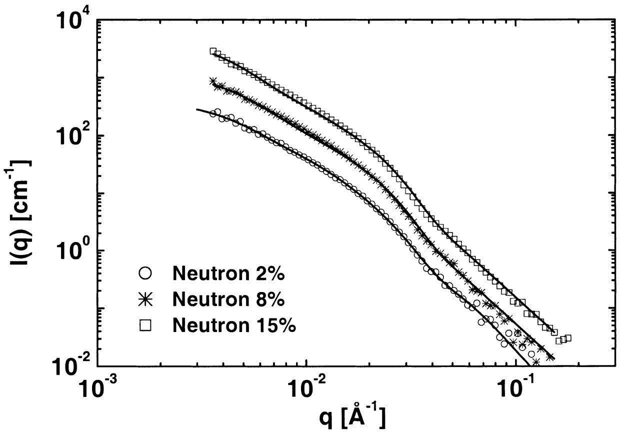

Fig. 2. Neutron intensities $I(q)$ (cm^{-1}) fitted with the Beaucage model for 2C99, 3C99 and 4C99.

Table 2

Structural parameters fitted with the Beaucage approach for the X-ray and neutron measurements on the silica-filled samples. Error bars on z and $R_{g,cl}$ mount up to 100% from the limited q-range whereas $R_{g,p}$ is accurate to 5%. The accuracy on d_{cl} and d_p is 2%. The headers x and n stand for X-ray and neutron data, respectively

Sample	ϕ	z		$R_{g,cl}$ (Å)		d_{cl}		$R_{g,p}$ (Å)		d_p	
		x	n	x	n	x	n	x	n	x	n
2C99	0.02	42	19	492	358	2.5	2.5	124	124	3.28	3.28
3C99	0.08	35	24	457	393	2.5	2.5	124	124	3.28	3.28
4C99	0.15	36	35	463	457	2.5	2.5	124	124	3.28	3.28
2V99	0.08	21		471		2.4		150		3.28	
5C99	0.08	47		515		2.5		124		3.28	
7C99	0.08	41		497		2.5		124		3.28	
3V99	0.15	24		538		2.4		150		3.28	
6C99	0.15	43		487		2.5		124		3.28	

(111 Å) [22] and the specific surface (125 Å) values of the parent unmodified VN2. The aggregation number z is given by the ratio of H_1 to H_3. The full comparison between the 2 probes, however, is only possible for 2C99, 3C99 and 4C99. Here, the quoted values for z and radius of the aggregates are virtually identical in view of the accuracy of the data. The differences by approximately a factor of 2 are due to the different low q-regime. The smallest achieved q-vector is in all too large to determine z or $R_{g,cl}$ unambiguously. Therefore, they should be merely considered as lower estimates.

In contrast to SANS the SAXS data were not absolutely calibrated, since the main purpose of these experiments was only to extract the structural parameters of the silica, i.e. its q dependence. They were shifted to overlap with SANS. An independent calibration is obtained from the subtraction procedure to obtain the chain scattering as will be discussed later.

5. Polymer characterization

Following the conclusions drawn in Section 4, that our reinforced networks can be treated as filled by an effective 1-component filler, the scattering of the labelled samples is described by Eq. (15) and the chain scattering is determined from it by the following steps:

- Determination of the SAXS-intensity of the sample and description of the q-dependence by a Beaucage-fit according to Eq. (18).
- Subtraction of the SAXS-intensity, multiplied by a prefactor F, interpreted as the phase scattering of the sample. The prefactor will be determined in such a way that the best agreement with the expected RPA-structure factor of the chain mixture results as

  $$I_{chain} = I_{tot} - FI_{ff} \tag{19}$$

  Starting with a properly calibrated intensity (to unit volume) I_{tot}, Eq. (19) will allow to access I_{chain} as well as the product FI_{ff} with the same level of calibration.
- Check and discussion of the obtained parameters of the chain scattering resulting from the absolutely calibrated SANS data.
- Discussion of the estimated values for the effective average scattering length $b_{f,av}$ of the filler.

For the description of the chain scattering a small Flory–Huggins parameter $\chi = 3.23 \times 10^{-4}$ had to be introduced to take into account a small H-D interaction in PI. The value was obtained from the unfilled blend and used for the description of the filled system. S_{RPA} per polymer molecule then reads for a blend of polymers of equal molecular weight M_w with monomer number N_w

$$S_{RPA} = \Phi_3 \Phi_4 g_D(q) N_w \frac{1}{(1 - 2\chi N_w g_D(q) \Phi_3 \Phi_4)} \tag{20}$$

The extraction procedure according to Eq. (19) is then performed by a least square fit of I_{chain} expressed by Eq. (20) with the factor F and the prefactor of the Debye-function g_D [23] as parameters to be fitted. To avoid problems due to the interdependence of the prefactor and the values of the radius of gyration for even slight noisy data at small q the value of R_g of the chains entering in g_D has been fixed to the best estimate of $R_g = 146$ Å according to the M_w of the polymers involved in the experiment and C_∞. It scales perfectly to the 142 Å already found by Westermann [24] for a polyisoprene with $M_w = 190{,}000$. The validity of the applied procedure and the basic concepts of our approach is proved by the very good description of the extracted chain scattering by the above discussed RPA function in Fig. 3. As expected the chains show a perfect random walk behavior. The residuum of the description of the total scattering intensity of the labeled systems by the sum of RPA- and Beaucage-contributions differs from zero only at the smallest q-values. The shape of the obtained q-dependence is probably related to particle–particle or cluster–cluster-correlations evidently not included in the used Beaucage description.

The observation of Nakatani et al. [8] that considerable shrinking of the chain in the presence of fillers of

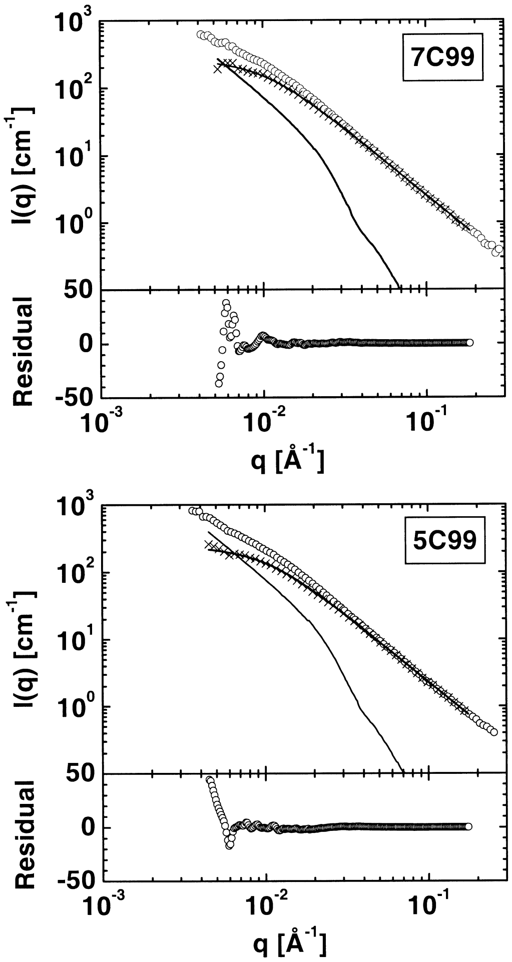

Fig. 3. Total absolute intensity (cm^{-1}), extracted polymer matrix intensity and extracted rescaled filler intensity for 5C99 (upper figure) and 7C99 (lower figure). The samples have different D-PI content but same filler volume fraction $\phi = 0.08$. The residual only is non-zero at low q and the Debye nature of chains is proven to a good extent.

comparable size to the chain dimensions takes place could not be confirmed from our data.

The obtained phase scattering allows also an estimation of the effective scattering length density of the silica. The experimentally obtained value from Beaucage fits with $\approx (1.8-1.9) \times 10^{10}\ \text{cm}^{-2}$ with some 30% accuracy from the various samples, is roughly 60% of the expected density for silica ($3.1 \times 10^{10}\ \text{cm}^{-2}$). Similar results are obtained from the SANS data of the unlabeled samples. This discrepancy could be due to empty ‘pockets’ in the open silica structure or which were at least inaccessible for the polymer chain, without affecting the conclusion of a single-phase behaviour.

This affects of course the theoretical matching conditions to be about 75H/25D instead of the formerly estimated 56H/44D ratio as envisaged in this study. The different labelling in the 2 samples (i.e. 10% lower) should therefore imply a different scattering contribution of the filler in the matrix, although in both cases the matching composition is never met. However, the trend of a smaller phase contribution for lower D content is clear from Fig. 3 in which the top curve for sample 7C99 (34D) shows less parasitic phase scattering than the lower one from 5C99 (40D).

The estimation of the ‘empirical’ scattering length for silica can be clarified by an hypothetical Guinier-like scattering at small q from z-times aggregated primary particles of a volume given by its radius of about 124 Å and partly from the cross-over functions. The Guinier level of the elementary particle is only of the order of a few percent ($\approx 1/z$) and does not interfere. The re-scaled SAXS forward scattering in Fig. 3 asymptotically yields $1458-1670\ \text{cm}^{-1}$ at $q = 0$ for $\phi = 0.08$ and z-values of 41 and 47 as in Table 2 relying on the theoretical scattering length density. This level increases to $\approx 3080\ \text{cm}^{-1}$ if the reduced value is used. If the radius of gyration is to be around 500 Å for the clusters the amplitude of scattering should have ideally dropped to approximately 2/3 of its zero-q value at $q_{\text{guinier}} \approx 1/R_{\text{g,cl}} = 0.002\ \text{Å}^{-1}$. The extrapolation of the mass-fractal region yields $\approx 2000\ \text{cm}^{-1}$ which agrees better with the reduced scattering length.

As an additional consistency test Table 3 summarizes the prefactors for the Debye-function g_{D} in Eq. (20) obtained from the extraction procedure compared to the estimated intensities from the molecular weight of the chains. The obtained values are qualitatively and almost quantitatively close to the expected values and confirm basic concepts and experimental and evaluation procedures. These data show also that the agreement between 2 different spectrometers (SANS-1 and SAND) is within expectation (10%) and uncertainties are associated with the calibration standard.

Summarizing the results and discussions it can be concluded that the derived additivity of phase and chain scattering could be quantitatively confirmed. Additionally, the failure of the realization of a complete matching of the phase scattering attempted by the design of the experiment could be explained by a deviating effective scattering contrast of the filler. Within the accuracy of the experiment a description of the phase scattering by the more elaborate 2-component filler turned out to be not necessary in the case of the investigated system.

Table 3
Estimated and fitted prefactors in the extraction procedure for the effective 3-component model (cm^{-1}). The calculated prefactors are obtained from Eqs. (15) and (20). Due to calibration methods small differences are possible between several instruments. The quality of agreement is, however, good and within the inherent accuracy of intensity calibration and sample filling degrees

Sample	I^{th}	I^{fit}
2V99	357	315
5C99	357	247
7C99	334	273
3V99	329	352
6C99	329	299

6. Conclusion

For the first time the extraction of experimental SANS scattering functions of the polymeric phase in the undeformed state has been performed for an effective 3-component system with fractal properties in absence of composition matching. A parallel X-ray study provided information on the filler structure and confirmed the positive complementarity of the 2 techniques. A novel approach for scattering from composites was presented and modified for fractal fillers in a labeled sample. It was experimentally shown that reliable structural details on both soft and hard phases in close-to-industrially relevant composites can be obtained from the synergy of 2 scattering probes, exploiting all possible contrasts. This work provides the basis for the investigation of the chain scattering under uniaxial load which is the subject of a forthcoming publication.

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