Mechanics of filled rubbers from a molecular point of view

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CHAPTER 3: REINFORCEMENT OF SILICA NANOCOMPOSITES


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3.1 Abstract

Particulate fillers are often used to enhance the properties of soft materials; polymer composites often contain nanometer-sized particles to improve reinforcement, for example. The rationale for using nanometer-sized particles remains unclear, however, and classical micromechanical models cannot account for a scale dependent reinforcement. The systems studied here reveal that the reinforcement increases with decreasing filler size. A new relation is proposed, based only on the particle size, volume fraction, and relative moduli of filler and matrix that describes the experimental results for reinforcement of both filled rubbers and a model system.

3.2 Introduction

Soft materials are often made up of particles dispersed in a continuous matrix, where the concentration and size of the filler particles has a profound effect on the physical properties. The addition of filler particles such as carbon black or silica to a polymer matrix, for example, changes the linear and non-linear mechanical behavior of the resulting composite material.[59,101] For filled rubbers, the linear shear modulus of the filled material increases by more than an order of magnitude over that of the bare rubber. This stiffening, called reinforcement, is defined as the normalized change in shear modulus at volume fraction $\phi$ of fillers compared to that of the unfilled polymer: $R(\phi) = G(\phi)/G(\phi = 0) - 1$, with $G$ the linear shear modulus. Numerous micromechanical models exist for composite materials that predict $R(\phi)$ on the basis of the mechanical properties of the constituent materials and their respective volume fractions.[102–104] Such models are based on classical elasticity theory, however, which is size-independent, so that they cannot account for a dependence of composite mechanical properties on the size of the fillers. This strongly contradicts the generic observation that nanoparticles with a high surface-to-volume ratio provide the highest reinforcement.[62,105–107] One recent study demonstrated and explained a size dependent deformability of liquid inclusions in soft matrices using a modification of Eshelby’s theory, but no such explanation exists for size-dependent elasticity of systems with hard inclusions in a polymer matrix. [108] In this work, the effect of rigid filler size on reinforcement of polymer
composites in industrial composite materials and a model system is investigated systematically.

3.3 Materials & methods

Filled rubbers
In total, five different types of filled rubbers were used. Two of them, are Styrene Butadiene Rubber (SBR, ρ =140 kDa, vulcanized) based nanocomposites with different rubber functionality (see section 2.1 in Chapter 2) filled with precipitated silica nano-particles. The three other filled rubbers are Acrylonitrile Butadiene Rubber (NBR; ρ =250 kDa, vulcanized), loaded with silica particles of different specific surface areas. Further details of these materials can be found section 2.1 in Chapter 2.

Model system
Polyvinyl Alcohol (PVA, hydrolyzed at 99-100% and a molecular weight of 86 kDa) is provided as a powder by Acros Organics. The powder is dissolved (4 wt %) in distilled water by mixing with a stirring bar at 95 °C for 3 hours. The borate is obtained by dissolving sodium tetra borate (Sigma Aldrich) in distilled water (4 wt %). For some measurements the mass fraction of 4 wt % was decreased in order to decrease the shear modulus of the matrix of the model system (Figure 3-7b). The gel is finally formed by mixing 2 g of solution of borate with 8 g of solution of PVA. The polystyrene beads are Dynoseed ® TS 500, TS 250, TS 140, TS 80 and TS 40 with radii of 250, 125, 70, 40 and 20 µm, respectively.

Rheological measurements
Oscillatory measurements were carried out with an Anton Paar Physica MCR 300 rheometer mounted with the parallel plate geometry. For measuring the filled rubbers the diameter of the geometry was 5 mm. Samples were cut in shape of disks with a thickness about 2.5mm. Loctite glue was used at sample and parallel plates in order to avoid wall slip during the measurements.[109] For the experiments with the model system the geometry was the same but with a diameter of 25 mm, and both of the surfaces were rough to avoid also any wall slip. Data were obtained in the linear regime. We measure here the complex modulus G*, which is found to be frequency independent and, because G' >> G", is equated to the shear modulus at low strain amplitude.[110]
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*Transmission Electron Microscopy and elemental mapping of silica aggregates*

Nanocomposites were imaged with transmission electron microscopy (TEM) and analyzed to determine the silica aggregate size. The nanocompounds were sectioned to a thickness of around 50 nm with an ultracryotome at −60°C using a diamond knife. TEM images were taken by operating a JEOL JEM 1400 microscope with an accelerating voltage of 120kV, which was maintained constant for all samples. To obtain sufficient statistics for aggregate size analysis, a large number of aggregates (~ 4000 aggregates per sample) were taken from different locations within each ultrathin cryosection. All the micrographs were taken with constant electron beam intensity and at an optimum magnification of 5000X.

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**Figure 3-1.** (a) SAXS spectra I(q) for the SBR samples (φ=0.16 and 0.24). The inset shows the Kratky representation of these same spectra. The aggregate size (r_{agg}) is found at the abscissa corresponding to the maximum of the curve. (b) r_{agg} results from Small-Angle X-Ray scattering (SAXS) analysis of silica/SBR samples loaded with 16 % vol. and 24 % vol. of silica fillers shown (filled columns) with the r_{agg} results from TEM image analysis (patterned columns). (c) TEM image of silica (1.6 vol %)/NBR nanocomposite including 15 nm diameter silica nanofillers (specific surface area: 175m²/g) and (d) elemental mapping image of the same region showing Si and Zn in green and red color, respectively.
Microstructural analysis of silica aggregates

In this work, silica microstructure is given by the mean aggregate size ($r_{\text{agg}}$) at different volume fractions. A thresholding routine is used to highlight aggregates against the rubber background in the TEM images and obtain particle analysis for calculating aggregate area and size (see 2.3 in Chapter 2). In order to compare the microstructural differences across composite samples the same thresholding parameters were kept constant. The output of the image analysis includes projected area ($A$), perimeter, and locational information of each aggregate identified in the image. The projected areas for all aggregates taken from a particular sample were pooled and averaged to calculate the average aggregate radius ($r_{\text{agg}}$).

3.3.1 Aggregate size measurement

TEM comparison with SAXS measurement

As a benchmark for the analysis aggregate size measurements from TEM are compared with those derived from Small-angle X-ray scattering SAXS (Beam line ID26 (ESRF Grenoble), wavelength 12.4 keV and distance between sample and detector is 7m., more information about the derivation can be found in ref [38]) for two types of SiO$_2$/SBR samples with different filler concentration (Figure 3-1). The agreement between values from TEM and SAXS for these samples demonstrates that the quantitative aggregate analysis is robust. Finally, the presence of strongly scattering ZnO particles (which have a size in the range of the aggregates) contribute to the SAXS spectra for NBR composites, so it was not possible to arrive at any meaningful aggregate size from these data. Therefore, TEM, coupled to energy dispersive X-ray (EDX) analysis, was necessary to segregate ZnO particles and only analyze sizes of silica aggregates (Figure 3-1(c) and (d)).

Polydispersity of the aggregates and aggregate size-volume fraction relation

The fillers in the real rubbers were found to be highly polydisperse (Figure 3-2a), with an average aggregate radius, $r_{\text{agg}}$, of ~ 40-100 nm, depending on the size of primary silica used. The radius of the aggregates is found to be independent of the volume fraction of silica (Figure 3-6b of the main text). As previously mentioned (see 2.1 in Chapter 2), all the filled rubber samples used in this article are provided by industrial partners who prepare these samples in internal mixers. The effect of
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this mixing process on aggregates is not clear and is beyond the scope of this article. Nevertheless it is possible to provide initial insights regarding the silica aggregation during mixing.

Figure 3-2. (a) Histogram showing the aggregate area distribution of silica (0.016 % vol.) / NBR nanocomposite. (b) SEM picture of aggregates (Zeosil 1165 MP) as provided by the manufacturer, prior to mixing.

The size of the silica added to the polymer is typically of the order of 100 µm, which is 1000 times larger than the final aggregates or the primary particles as quoted by the manufacturer (Figure 3-2b). Others have shown that these large silica particulates are broken down during mixing and potentially grow again via re-agglomeration.[111] This phenomenon was addressed in a recent study of the parameters influencing the structure of the filled material during mixing.[111] In that study it was shown that the radius of the aggregates increases with volume fraction if the parameters of mixing are kept constant, but that an increase of the power of mixing on the other hand decreases the radius of the aggregates. In the present work there is a constant radius of the aggregates that is independent of the volume fraction. The previous study indicates that this result follows from a rather complicated process. However, a constant size (i.e. independent of φ) has been observed in other filled rubbers.[38]

3.4 Results and discussion

Monodisperse polystyrene microspheres, which do not aggregate, are used in the model system (see section 3.3). For the industrial compounds, the primary
nanoparticles aggregate into clusters, and their average aggregate size ($r_{agg}$) is measured using TEM. Several of the fillers contain zinc oxide, which precludes SAXS measurements. TEM sizing was validated against SAXS in the industrial rubbers where no zinc oxide was present (Figure 3-1b). A scaling for $R(\varphi)$ is obtained that describes the size dependence of the reinforcement for all studied systems. The scaling incorporates an explicit dependence on the size of the filler or filler aggregate and the mechanical contrast between the filler and the matrix material. This scaling captures the filler-size-dependent reinforcement of composite materials and provides the underlying rationale for the use of nanosized filler particles in such materials. The first industrial composite is an acrylonitrile butadiene rubber (NBR) matrix filled with 15, 20, and 28 nm primary size silica particles. The chemistry is varied by using an additional industrial composite consisting of a styrene butadiene rubber (SBR) matrix filled with silica particles. The model system consists of a polymer gel, polyvinyl alcohol (PVA) crosslinked with Borax,[112] reinforced with polystyrene beads of radii ($r_b$) ranging from 20 to 250 μm.

![Figure 3-3. Reinforcement (R) versus volume fraction for (a) the industrial rubbers (SBR and NBR) with fillers of varying sizes and (b) the model system (PVA gel filled with polystyrene beads of radius ($r_b$)). The grey and black lines correspond to the Einstein-Smallwood Equation (ESE) and the Christensen-Lo model, respectively. Additional information about the Christensen-Lo model can be found in the Appendix I. The mechanical contrast between the moduli of the fillers and the matrix is $\sim 10^6$ for the model system (PVA gel: $G \sim 10^3$ Pa; polystyrene: $G \sim 10^9$ Pa) and $\sim 10^3$ for the filled rubbers (SBR and NBR rubber: $G \sim 10^6$ Pa; silica: $G \sim 10^9$ Pa)](image)

The reinforcement measurement shows that for the industrial rubbers $R(\varphi)$ at any fixed value of $\varphi$ is largest for the samples with the smallest silica
primary particle (Figure 3-3a). The model system, despite its simple microstructure, qualitatively exhibits the same mechanical behavior as the industrial rubbers (Figure 3-3b): a larger reinforcement is observed for smaller particles. Classical elasticity theory on the other hand supposes that (i) the filler size is irrelevant and (ii) the reinforcement is a function of $\varphi$ only. In both systems, the Einstein-Smallwood Equation (ESE, $R = 2.5\varphi$) no longer describes the reinforcement when $\varphi$ is greater than 0.15, as filler size clearly begins to play a role. An alternative model for reinforcement is the Christensen-Lo model, which uses a mean field approximation (a filler particle surrounded by a polymer layer embedded in the bulk composite material[103,113] - see Appendix I). This model clearly underestimates the reinforcement (Figure 3-3), though it can be forced to fit the reinforcement-volume fraction curve for a single filler type (size) by incorporating an effective volume fraction (the volume fraction times a proportionality factor), which is attributed to the fractal nature of the aggregates of the silica nanoparticles.[58,113,114] Even with this parameter, however, the filler-size-dependent elasticity cannot be captured. Hence, the challenge is to develop a composite elasticity theory that accounts not only for filler volume fraction $\varphi$ but also for filler size $r_{b,agg}$ in describing the reinforcement of a composite material.

Figure 3-4. Filler-size dependence of the reinforcement of the model system: (a) reinforcement versus the inverse of the radius of the beads for different volume fractions. The red lines are linear fits with slope $a$. Inset: Slopes $a$ as a function of $\varphi^3$. Here, another linear dependence is apparent so the data can be described by $R = 2.5\varphi + C\varphi^3/r_b$. (b) Reinforcement versus the rescaling parameter derived in Figure 3-4(a) for both the model system and the filled rubbers (aggregate size measurement for filled rubbers in Figure 3-6; $r_{b,agg}$ is the radius of beads or aggregates depending on the system considered). The reinforcement data used are the same as in Figure 3-3. The line has unity slope. The values found for C are 73 and 20 microns for NBR and SBR respectively.
To further explore the filler-size-dependent reinforcement, it is plotted as a function of $1/\tau_b$ at constant $\phi$ for the model system, for which the particle size is well-defined. It is evident that reinforcement increases linearly with the inverse radius of the filler particles (Figure 3-4a). The lines in Figure 3-4a are of the form $R = 2.5\phi + a/\tau_b$, which is the ESE reinforcement plus a size-dependent factor $a/\tau_b$, with a varying as $\phi^3$ (Figure 3-4a inset). After characterization of the aggregate size in filled rubbers from TEM imaging (Figure 3-6 and section 3.3.1) a similar correction for the reinforcement is obtained of the form $R = 2.5\phi + b/\tau_{agg}$ and a similar analysis shows that $b$ correspondingly varies as $\phi^3$. By plotting the reinforcement data for all systems on the same graph, Figure 3-4b shows that the same reinforcement relation $R = 2.5\phi + C\phi^3/\tau_{b,agg}$ accurately describes the size-dependent-reinforcement for the model and industrial systems, where $C$ is a constant with dimensions of length. This correction can then be viewed as the expected $\phi^2$ correction to the ESE relation multiplied by the specific surface area $S$ ($\text{surface area per unit volume}$) of the filler, $S = 3\phi/\tau_{b,agg}$, yielding $R \sim \phi^2 S$.

![Figure 3-5](image)

**Figure 3-5.** Illustration of different elements model used for finding $\phi^3/r$. Blue balls represent the aggregates and they are linked with elastic springs.

A similar modulus scaling with roughly $\phi^3$ has been observed for percolated networks;\[115,116\] however, TEM images suggest that the systems studied here are not percolated (Figure 3-6a). Furthermore, recent work from Chen
et al. [117] showed that the systems considered in the present work do not percolate below \( \varphi = 0.35 \). Therefore, a starting point for developing a length-scale dependent elasticity for reinforcement may be obtained from the following considerations: (i) in the ESE model, the 2.5 \( \varphi \) term arises from hydrodynamic effects;[118] (ii) the first interaction term is expected to scale as \( \varphi^2 \) (for pairwise interactions), as in the Guth-Gold-Einstein relation \( R = 2.5\varphi + 14.1\varphi^2 \). The size dependence must therefore enter through the mechanism of interaction. If one imagines a set of spring-like forces (transmitted via the polymer network) between neighboring aggregates whose number is determined by the available surface area, the first-order representation of such a spring-like contribution to the elastic response would scale as the surface-to-volume ratio, which is \( \varphi/r_{b,agg} \) in correspondence with the observed \( \varphi^3/r_{b,agg} \) dependence.

Figure 3-6. Microscopic characterization of the silica aggregates in industrial NBR composites: (a) TEM image analysis from a 50 nm thick slice showing aggregate regions distinguished from NBR matrix (red color borders). The number and coverage area of the aggregates \( (N_{agg} \text{ and } A \text{ respectively}) \) is obtained from these pictures. Assuming circular shapes, the radius of the aggregates \( r_{agg} \) are defined by \( r_{agg} = (A/\pi N_{agg})^{1/2} \). (b) Measurement of the radii of the aggregates \( (r_{agg}) \) as a function of volume fraction. The aggregate size does not depend on \( \varphi \). The inset shows the radius of the aggregates as a function of the radius of the primary particles at \( \varphi = 0.14 \). Error bars are standard errors of the mean from \( N > 4000 \) aggregates. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

One way of understanding the \( \varphi^3 \) term microscopically is to realize that upon increasing \( \varphi \), the radial distribution function \( g(x) \) develops a peak that corresponds to the average distance between nearest neighbours, implying also an effective
potential of the mean force between two particles, \((V_{\text{eff}}(x_{\text{min}}))/kT = -\log[g(x_{\text{max}})]\) [119] (which is valid if the matrix elasticity is affected by the silica aggregates as shown in Ref. [10]); \(V_{\text{eff}}(x)\) takes into account all many-body effects mediated by the polymer chains, including bridging, in a mean-field manner. This allows one to define a spring constant \(\kappa = ((d^2 V_{\text{eff}})/(dx^2))_{r_{\text{min}}}\) parameterizing the interaction strength between neighboring particles, every bond being a spring of length, \(d = 2r_{b,\text{agg}} + x\), where \(r_{b,\text{agg}}\) is the particle size and \(x\) is the separation between two particles (Figure 3-5). The overall elastic modulus of such an assembly of interacting particles can be evaluated considering the energy necessary to macroscopically deform the material by a strain \((\gamma)\), implying that each spring is stretched by a relative amount \(\approx dy\). If the springs can be considered to be independent (which is a rough assumption, but it is very difficult to do better at the level of simple scaling arguments), the total elastic energy is given by total number of springs \(n_{b}N/2\) multiplied by the energy of each spring, where \(n_{b}\) is the number of nearest neighbors per particle and \(N\) the total number of particles. The total elastic energy density (per volume \(V\)) can be derived as \(\approx \kappa n_{b}(N/V)(d\gamma)^2\) and the shear modulus can be calculated as the second derivative of energy density with respect to \(\gamma\) as \(G \approx \kappa n_{b}(\varphi/r_{b,\text{agg}}^3)d^2\), where \(N r_{b,\text{agg}}^3/V \approx \varphi N\) is used. If the neighbors are not too far from each other, \(d \approx 2r_{b,\text{agg}}\), leading to \(G \approx \kappa n_{b}(\varphi/r_{b,\text{agg}})\). This recovers the proportionality to \(S\), the specific surface area of particles per unit volume. Further, the number of neighbours \((n_{b})\) can be estimated from the integral of the peak of the radial distribution function Ref. [120]; for not-too-dense systems, \(g(x_{\text{max}}) \approx 1 + b\varphi\) (a Taylor expansion about infinite dilution), where \(b\) is a coefficient that depends on the interaction (e.g. \(b \approx 3\) for hard spheres).[121] It then follows that the first non-linear term in volume fraction is \(n_{b} \approx \varphi^2\). Combining these relationships leads to \(G \approx \kappa n_{b}(\varphi/r_{b,\text{agg}}) \approx \varphi^3/r_{b,\text{agg}}\), which is the scaling derived from the experimental measurements.

Whether arriving at \(R \sim \varphi^3\) scaling via the microscopic derivation or intuitive expansion of ESE for non-interacting particles with a particle-interaction term, both lead to the relation, \(R = 2.5\varphi + C\varphi^3/r_{b,\text{agg}}\). The reinforcement at high volume fraction can be physically understood as a coupling between volume and surface effects, which explains the filler-size-dependent reinforcement in this regime, and the magnitude of \(C\) is the upper limit for separation between aggregates within the polymer matrix.
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Figure 3-7. Dependence of C on the mechanical contrast between filler and matrix: (a) Linear shear modulus of the PVA gel with different concentrations of crosslinker (Borax). (b) Evolution of C with the moduli contrast between fillers and matrix. The grey line shows the fit with slope $d = 25$ nm.

In the rescaling presented here, C is the only unknown parameter. It is a proportionality constant with units of length that depends on the type of system. The reinforcement of any filler/matrix system is expected to scale with the ratio of the modulus of the filler to that of matrix, because a soft filler does not reinforce a composite to the same extent as a hard filler at the same volume fraction, and the reinforcement should go to zero when the moduli of filler and matrix are equal. Therefore, the value of C should scale with the ratio $G_f/G_0$, with $G_f$ the modulus of the bulk filler material (e.g. silica or polystyrene) and $G_0$ is the modulus of the unfilled matrix. This is indeed observed when the crosslinking in the model system is tuned (see Figure 3-7a) to modify $G_0$. Consequently $R = 2.5\varphi + \delta \frac{(G_f)}{G_0} \varphi^3/r_{b,agg}$ with $\delta = 25$ nm for all systems studied (Figure 3-7b), where $C = \delta(G_f/G_0)$. C then defines a physical length scale that can be interpreted as the maximum spacing between aggregates for which the $\varphi^3$ term will contribute to reinforcement of the composite material (Appendix I). One can calculate a required filler (or aggregate) “density” as $1/C$, which decreases as the mechanical contrast between the filler material and matrix increases, with the maximal filler density equal to $1/25$ nm when the modulus contrast is unity.
3.5 Conclusions

In this article the filler size-dependent reinforcement was studied for industrial rubbers as well as for simplified model system with well-defined beads as fillers. While it is a common, yet puzzling, observation that smaller filler particles are better reinforcing agents,[62,107] this effect has been quantified here and a scaling law for the filler-size dependence of the reinforcement of composites was derived. This scaling law is a first, but critical, step to developing new theories for predicting reinforcement of composites materials. It is sufficient to account for the filler-size dependent reinforcement phenomenon; no other terms in an expansion in volume fraction are needed for the (rather large) volume fraction range studied here. In addition, only a single parameter $C$, which is proportional to the filler to matrix modulus ratio, is necessary to rescale all data for a given combination of filler and matrix materials once the filler (or aggregate) size is known. Finally, it is worthwhile to mention that a variety of systems and chemistries were studied in this work, strongly suggesting that the rescaling presented here is universal and reveals a fundamental insight as to why small fillers are commonly and efficiently used to achieve maximal reinforcement in composite polymer materials.
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3.6 Appendix I

3.6.1 The Christensen Lo Model

![Figure 3-8](image)

The Christensen-Lo model is based on the equivalent medium theory. This technique considers a single filler (1), a pure polymer layer surrounding it (2), and an effective medium around the polymer layer (3). This effective medium includes the combined effect of all the other fillers embedded in the polymer matrix. The modulus of this medium is the modulus of the overall material. Continuity of the displacement and the stress at the filler/polymer and polymer/equivalent medium interfaces is assumed. This yields a second order equation for the reinforcement [103,122]:

\[
\begin{align*}
A \left( \phi, \nu_p, \nu_e, \frac{G_p}{G_e} \right) (R+1)^2 + 2B \left( \phi, \nu_p, \nu_e, \frac{G_p}{G_e} \right) (R+1) + C \left( \phi, \nu_p, \nu_e, \frac{G_p}{G_e} \right) &= 0 \\
A &= 8 \left( \frac{G_p}{G_e} - 1 \right) (4 - 5 \nu_e) \eta_1 \phi^2 - 2 \left( 6 \left( \frac{G_p}{G_e} - 1 \right) \eta_1 + 2 \eta_1 \eta_2 \right) \phi^2 + 252 \left( \frac{G_p}{G_e} - 1 \right) \eta_2 \phi^2 - 50 \left( \frac{G_p}{G_e} - 1 \right) (7 - 12 \nu_e + 8 \nu_e) \eta_2 \\
P &= -2 \left( \frac{G_p}{G_e} - 1 \right) (1 - 5 \nu_e) \eta_1 \phi^2 + 2 \left( 63 \left( \frac{G_p}{G_e} - 1 \right) \eta_1 + 2 \eta_1 \eta_2 \right) \phi^2 - 252 \left( \frac{G_p}{G_e} - 1 \right) \eta_2 \phi^2 + 75 \left( \frac{G_p}{G_e} - 1 \right) (3 - \nu_e) \nu_p \eta_1 \phi^2 \\
P &= 4 \left( \frac{G_p}{G_e} - 1 \right) (5 \nu_e - 7) \eta_1 \phi^2 - 2 \left( 63 \left( \frac{G_p}{G_e} - 1 \right) \eta_1 + 2 \eta_1 \eta_2 \right) \phi^2 + 252 \left( \frac{G_p}{G_e} - 1 \right) \eta_2 \phi^2 + 25 \left( \frac{G_p}{G_e} - 1 \right) (\nu_e - 7) \eta_2 \\
P &= -7 + 5 \nu_e \eta_1 \eta_2 \\
& \eta_1 = \left( \frac{G_p}{G_e} - 1 \right) (7 - 10 \nu_e) (7 + 5 \nu_p) + 105 (\nu_e - \nu_p) \\
& \eta_2 = \left( \frac{G_p}{G_e} - 1 \right) (7 + 10 \nu_p) (7 + 5 \nu_p) + 35 (1 - \nu_p) \\
& \eta_3 = \left( \frac{G_p}{G_e} - 1 \right) (8 - 10 \nu_e) + 15 (1 - \nu_p)
\end{align*}
\]
Here, \( \nu_f \) and \( \nu_0 \) are the Poisson ratios of the filler and the matrix, respectively, and \( G_f \) and \( G_0 \) the moduli of the filler and matrix, respectively. The Poisson ratios of matrix and fillers are respectively \( \sim 0.5 \) and \( \sim 0.2 \), and the modulus of the matrix is negligible compared to the modulus of the fillers (3 to 6 orders of magnitude smaller), so after some calculations this equation yields a general solution:

\[
(R + 1) \pm \sqrt{\frac{B'(\varphi)}{2A'(\varphi)}} - 4 \frac{A'(\varphi)C'(\varphi)}{A'(\varphi)}
\]

One of the solutions is negative and can be discarded for physical reasons, the other one is plotted in Figure 3-3 (a) and (b). In the end there are only three parameters that must be considered in the model: the Poisson ratios of both filler and matrix, and the volume fraction.

3.6.2 Determination of C for filled rubbers

\[ C \]

\[ \text{Figure 3-9. Filler-size-dependent reinforcement for filled NBR: (a) plot showing reinforcement versus the inverse of the radius for different volume fractions. (b) Slopes of lines in (a) as a function of the volume fraction of the filler beads. The solid line shows the cubic fit of this parameter; the inset illustrates the cubic dependence of reinforcement on the filler volume fraction.} \]

\[ C \]

C is determined for filled NBR as for the model system. The reinforcement (data in Figure 3-3a) is plotted as a function of the inverse of the radius of the aggregates, and then the slope \( a \) is fit to get \( C \). The value found is 73 microns for filled NBR. This method could not be applied for the SBR because the aggregate size is not varied at a given volume fraction. As stated in the main text, \( C \) is found to be 40
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microns for this sample, which is comparable to what is obtained for the NBR samples (73 microns).

3.6.3 The C parameter

The shear modulus of the composite material is given by affine theory (see the paper) as $G \approx b\kappa \phi^3 / r_{b/agg}$, where $b$ is a dimensionless prefactor related to the height of the first peak of the pair correlation function of nanoaggregates. The reinforcement is defined as $R = G(\phi) / G_0 - 1 \approx b\kappa \phi^3 / (r_{b/agg} G_0)$, where the last approximate equality considers only high volume fractions. Hence, the parameter $C$ is obtained as $C = b\kappa / G_0$, where $G_0$ represents the shear modulus of the pure rubber with no fillers. In the microscopic model, $\kappa$ represents the spring constant of the polymer-mediated interaction between two nanoaggregates and has dimensions [force/length], while $G_0$, by definition, has dimensions [force/length^2].

By introducing a generic length-scale $l$, $C = (b\kappa / l) / (G_0 / l)$. Here, $G_{loc} = b\kappa / l$ has the dimension of an elastic modulus, which measures the rigidity of nearest-neighbour nanoaggregate interaction over the length scale $l$. If one takes $l = l^*$ such that $G_{loc}(l^*) = G_0$, then clearly $C = l^*$. Therefore, $C$ represents the critical length scale or critical average mutual separation $l^*$ of two nearest-neighbour nanoaggregates for the elastic modulus of the nanocomposite to be equal to the elastic modulus of the pure rubber. In other words, the $\phi^3$ reinforcement vanishes, or reduces to ESE, if the aggregates are on average farther apart than the critical separation distance $l^*$. In the systems studied here the average separation between two nearest-neighbour nanoaggregates is $\sim 100$ nm, which is much less than $C (\sim 50 \mu m)$, and the effective modulus of the nanoaggregate array is much larger than that of the pure rubber.