Towards an understanding of filled rubbers

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Adding filler particles such as carbon black or silica to a polymer matrix profoundly changes the linear mechanical behavior of the resulting composite material [15]. This effect is widely used in many plastic and rubber materials all around us, yet a fundamental understanding of the mechanisms determining reinforcement is still lacking. For example, in filled rubbers, the linear shear modulus of the filled material routinely increases by more than an order of magnitude over that of the bare rubber. The reinforcement, defined as the change in shear modulus at volume fraction $\phi$ of filler particles compared to that of the polymer alone, can be written as $R(\phi) = G(\phi)/G(\phi = 0) - 1$, where $G$ is the linear shear modulus. Numerous micromechanical and homogenization models exist for composite materials [12–14] that predict $R(\phi)$ on the basis of the mechanical properties of the constituent materials and their respective volume fractions. However, since nearly all models are based on classical elasticity theory, they do not explicitly include a dependence of composite mechanical properties on the size (or size distribution) of the filler particles. When considering the experimental observation that nanoparticles (not micro or macro particles) with a high surface-to-volume ratio provide the most substantial reinforcement [32–35] at a given volume fraction, this highlights a gap in our fundamental understanding of composite system elasticity. Despite many earlier studies reporting filler-size-dependent reinforcement [25, 35], the underlying reason why smaller fillers lead to improved reinforcement is not clear.

In this chapter we investigate the effect of the fillers on reinforcement in a variety of real (industrial) composite materials wherein the sizes of primary particles were changed. For our compounds, the primary nanoparticles aggregate into clusters, and we measure their average aggregate size using transmission electron microscopy (TEM). We uncover a scaling for the reinforcement that captures the filler-size-dependent reinforcement of composite materials and provides a physical reason for the use of nanosized filler particles in such materials.
3.1 MATERIALS AND METHODS

Filled rubbers and model system

We use five different types of filled rubbers. The two first types of filled rubbers are the functionalized and non-functionalized rubbers introduced in Section 2.1.1. The three other filled rubbers are Nitrile Butadiene Rubber (NBR) ($\rho = 250$ kDa, vulcanized, provided by SKF®), filled with silica particules of radii 15, 20 and 28 nm. The model system is the filled Polyvinyl / Borax gel introduced in Sect. 2.1.2.

Measurements

The rheological oscillatory measurements were carried as introduced in Sect. 2.2.1 with a plate/plate geometry. For filled rubbers the diameter of the geometry was 5 mm and the samples were disks with a thickness about 2.5 mm stuck on each side to avoid wall slip with a Loctite 421 glue [10]. For the experiments with the model system the geometry was the same but we used a diameter of 25 mm and both of the surfaces were rough to avoid any wall slip.

3.2 REINFORCEMENT: STATE OF THE ART

3.2.1 The Einstein Smallwood Equation

The first model that aimed to understand the reinforcement is the Einstein-Smallwood equation [36]. Einstein did not work on filled rubbers but Smallwood adapted the well-known Einstein equation, valid for the viscosity of dilute suspensions to filled rubbers. For these systems the equation becomes:

\[
R = 2.5\phi
\]

(3.1)

This equation is valid for an infinitely dilute system and accounts for the individual contribution of the particles to the reinforcement. The adaptation of Einstein’s work was led further by Guth. The Guth Einstein equation [11] features a second-order term accounting for weak interactions $R = 2.5\phi + 14.1\phi^2$. 

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3.2.2 The effective medium theory and some associated models

During the mid-seventies, based on innovative mathematical tools (Eshelby tensor, effective medium theory), a new class of micromechanical models appeared [13, 37] that was used and improved over the next 30 years [12, 38]. To understand the new insights from these models, we briefly introduce one of them: the Christensen-Lo model. This model is an effective-medium theory as introduced in Chapter 1. It considers a single bead, with a layer of pure polymer surrounding it, embedded in an effective material that is a mixture of polymers and fillers. The continuity of stresses and deformations at the two interfaces then leads to an implicit equation:

\[ A(\phi)(R+1)^2 + B(\phi)(R+1) + C(\phi) = 0 \] (3.2)

Here, A, B and C are sums of rational powers of the volume fraction, which are derived for the general case in [13]. Considering that the modulus of silica fillers is several order of magnitudes higher than the modulus of the polymer matrix, A, B and C are only dependent on the volume fraction and the Poisson ratio of the silica (0.33) and matrix (0.5).

3.2.3 The concept of effective volume fraction

The concept of effective volume fraction is quite simple to understand. For filled rubbers, one needs to mix together particles and polymer. The particles are aggregating and polymer can be contained inside these aggregates. In the end, what is considered as an aggregate is not only silica or carbon black but also occluded polymer. This allows to introduce an effective volume fraction that is higher that the real volume fraction, defined as:

\[ \phi_{eff} = \alpha \phi \] (3.3)

More elaborate expressions of the effective volume fraction can be found in [39], but will not be discussed here. The effective volume fraction is in general used to force the fitting of data with effective-medium theories. As we will discuss below, this unfortunately has very little physical meaning.
3.3 Is the Volume Fraction Enough to Account for the Reinforcement of Filled Rubbers?

In order to answer this first question we measured the reinforcement for each of the systems introduced and compared them to the existing micromechanical models. These measurements show that at constant volume fraction, the modulus – and therefore $R(\phi)$ – increases with increasing filler content, and is largest for samples with the smallest filler size (Fig. 3.1, symbols).

![Figure 3.1: Reinforcement versus volume fraction for filled rubbers (A) and the PVA gel + polystyrene beads system (B).](image)

At low filler volume fraction the reinforcement is linear in $\phi$ and follows the Einstein-Smallwood equation $R = 2.5\phi$ that becomes exact in the limit of infinite dilution and in practice works very well for dilute systems [36] (Fig. 3.1, dotted line). This means that (i) there is no interaction between the fillers, as expected for low volume fractions, (ii) the filler size is irrelevant, and hence (iii) the reinforcement is a function of the volume fraction only. To the contrary, for higher volume fractions the Einstein-Smallwood relation is unable to describe the reinforcement. More elaborate models such as the archetypical Christensen-Lo model [13, 36] are commonly used for higher volume fractions. We
fit both models since it is not clear at which volume fraction the interactions, which are not taken into account by Einstein-Smallwood model, become important. The Christensen-Lo model does take such interactions between particles into account in a mean-field manner, which is the main difference between the two [13, 36]. While these models appear reasonable up to ∼ 0.1 volume fraction, they clearly do not fit for larger volume fractions (Fig. 3.1, solid and dotted lines). More importantly, the size dependence of reinforcement, especially obvious at higher volume fractions, is not at all captured by this model either. It is possible to force the Christensen-Lo model to fit the reinforcement-volume fraction curve for a single filler type (size) by incorporating an effective volume fraction, which is commonly attributed to the fractal nature of the aggregates of the silica nanoparticles [11, 15, 36, 39, 40]. However, even with an extra adjustable parameter, the size dependence cannot be captured. Clearly, an essential ingredient is missing in the micromechanical models as well. The underlying scale-free formalism of either the Einstein-Smallwood or Christensen-Lo model is simply unable to accurately describe the filler-size-dependent reinforcement. The key challenge is then developing a model that takes into account the size in addition to the amount of the fillers in predicting the elasticity of a composite material.

3.4 ACCOUNTING FOR THE SIZE DEPENDENCE OF THE REINFORCEMENT FOR THE MODEL SYSTEM

![Graphs](image)

Figure 3.2: (A) 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.

We now consider the model system, which is much simpler since it has no particle aggregation or network formation. We can plot the reinforcement as a function of the
radius of the filler particles at constant volume fraction (Fig. 3.2A). From this graph, it appears that the reinforcement increases linearly with the inverse of the radius of the filler particles. The lines in Fig. 3.2A are of the form: \( R = 2.5\phi + a/r \), which means that the particle size dependence can be taken into account by adding a correction factor \( a/r \) to the Einstein-Smallwood equation: the reinforcement is a function of both the volume fraction and radius of filler particles. The slope \( a \), in turn, is observed to vary as the third power of the volume fraction (Fig. 3.2B). This allows us to obtain a general expression of the reinforcement as \( R = 2.5\phi + C\phi^3/r \), where \( C \) is a constant with dimensions of length to ensure the homogeneity of the equation.

3.5 APPLICATION TO FILLED RUBBERS

To apply these findings to filled rubbers, we need to characterize the microstructure of these systems and especially the aggregate sizes. One way to characterize the filler size is to carry out Small-Angle X-ray experiments (SAXS afterwards). However, NBR samples contain zinc oxyde, which precludes the use of SAXS because ZnO scatters too much. In this section we will compare the results from SAXS and TEM (MPI Mainz) experiments, on SBR samples in order to validate our results and obtain the aggregate radius. For the NBR rubbers, we only use TEM.

3.5.1 Measuring the aggregate radius

TEM microscopy

As introduced in Chapter 2, the aggregate-size measurement using TEM follows two main steps. First, TEM imaging and localization of the aggregates is done (Fig. 3.3 A and B). Second, the number of aggregates and the surface they occupy are determined (Fig. 3.3.C). The results show that the radius of the aggregates is independent of the volume fraction (Fig. 3.3D). This check was done since it is known that in some systems, the final aggregate-size distribution results from the breakup of large aggregates during the compounding which is influenced by the volume fraction. A recent study by Bumm et al. [41] deals with the different parameters influencing the aggregate sizes during filled rubber processing. Two effects compensate each other: on the one hand increasing the volume fraction promotes the primary particles to meet each other and consequently form bigger aggregates. On the other hand, the mixing speed is increased with increasing volume fraction which leads to smaller aggregates.

Comparison of TEM and SAXS measurements
Figure 3.3: (A) TEM image analysis distinguishing aggregate regions from the NBR matrix (red color borders). (B) Each individual aggregate area is quantified for later analysis (e.g. average $r_{agg}$). (C,D) Distribution of aggregate areas as determined from the measurement. (E) Reinforcement versus the inverse of the aggregate radius for a volume fraction of 0.14.

As a benchmark for the TEM measurement, we can compare aggregate size measurements from TEM with those derived from SAXS for non-functionalized and functionalized samples with different filler concentrations (Fig. 3.4 C). The rough agreement between values from TEM and SAXS for these samples demonstrates that our quantitative aggregate analysis is robust.

3.5.2 The size dependence in filled rubbers

Knowing the aggregate size for all three NBR (model) rubbers at all volume fractions from TEM and the reinforcement via rheology, we can then plot the reinforcement as a function of the inverse radius of the aggregate size for different volume fractions (Fig. 3.5A). From this graph, it appears that again reinforcement increases linearly with the
Figure 3.4: (A) SAXS spectra for functionalized rubber and (B) SEM (Scanning Electron Microscopy) of the silica before compounding. (C) Comparison between SAXS and TEM results: functionalized SBR (grey columns) and non-functionalized SBR (black columns) samples loaded with 16% vol. and 24% vol. of silica fillers shown with the $r_{agg}$ results from TEM image analysis (patterned columns with same colour codes).

inverse of the radius of the filler particles at a given volume fraction. The linear fits (Fig. 3.5A) for each volume fraction show that the aggregate radius affects the reinforcement to different extents, based on the volume fraction of the fillers. The lines in Fig. 3.5A are again of the form: $R = 2.5\phi + a/r$, which means that the particle-size dependence can be taken into account by adding a correction factor $a/r$ to the Einstein-Smallwood equation; reinforcement is a function of both the volume fraction and radius of filler particles. The slope $a$ is a microscopic length scale that is on the order of the particle size; its value is observed to vary as the third power of the volume fraction (Fig. 3.3B). This allows us to obtain the same expression for the reinforcement as for the model system $R = 2.5\phi + C\phi^3/r$, where $C$ is a constant with dimensions of length to ensure the homogeneity of the equation; for this silica type, we find $C = 73 \mu m$. 

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Figure 3.5: Reinforcement versus inverse of the radius of the aggregate for different volume fractions for all NBR rubber systems investigated in this work. Symbols represent discrete volume fractions. Black lines are linear fits to each volume fraction. (B) Slope of the lines in (A) versus $\phi^3$; the solid line is linear fit.

3.6 A CORRECTION TO EINSTEIN-SMALLWOOD

Figure 3.6: Reinforcement versus the corrected Einstein-Smallwood model including the radius dependence. The data are the same as in Fig. 3.1. The black line has a unit slope. The values of C for the filled rubber samples are 40, 20, 73 $\mu$m for the non-functionalized, functionalized and NBR, respectively. The value for the model system is 12 mm.
Because we also measured the aggregate sizes for all SBR rubber samples, we implement the same rescaling to all the filled rubbers, disregarding any changes in polymer matrix (SBR or NBR) or polymer chemistry (end-functionalized or not). The result is shown in Fig. 3.6, which clearly shows that our new expression for the reinforcement accurately describes the reinforcement behavior in the other NBR and the SBR rubbers as well: the data from all systems lie on the same curve with unit slope.

3.6.1 Why $\phi^3/r$? (collaboration with Alessio Zaccone - TU Munich)

![Figure 3.7: Representation of the different elements of the model. The red circles represent aggregates linked together by springs.](image)

The scaling we employ here includes a third-order term in the volume fraction and not the expected second-order term. A similar modulus scaling with roughly $\phi^3$ has been observed for percolating networks [42, 43]; however these are quite different compared to our polymer-filled composites, which do not appear to be percolated (Fig. 3.2). Therefore, a starting point for developing a length-scale dependent elasticity for reinforcement may be obtained from the following considerations: (i) the 2.5$\phi$ term arises from the individual contributions of the filler particles in the dilute regime, where the particles do not interact [36]. (ii) The first interaction term is expected to scale as $\phi^2$ (for pairwise interactions), as reflected in the Guth-Gold-Einstein relation. The size dependence must therefore enter through the mechanism of interaction. If we imagine a set of spring-like forces (transmitted via the polymer network) between neighboring aggregates whose density is determined by the available surface area, the first-order representation of such a spring-like contribution to the elastic response would therefore scale as the surface-to-volume ratio, which is $\phi/r$, leading to the observed $\phi^3/r$ dependence.

One way of obtaining this result microscopically is to realize that upon increasing $\phi$, the radial distribution function $g(x)$ develops a peak that corresponds to the average
distance between nearest neighbors, also implying an effective potential of mean force between two particles,

\[
V_{\text{eff}}(x_{\text{min}})/kT = -\log[g(x_{\text{max}})] \quad [44]
\]

(which is valid if the matrix elasticity is affected by the silica aggregates as shown in [25]): \( V_{\text{eff}}(x) \) 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 \( \kappa = (d^2V_{\text{eff}}/dx^2)|_{x_{\text{min}}} \) parameterizing the interaction strength between neighboring particles, every bond being a spring of length \( R_0 = 2r + x \), where \( r \) is the particle size and \( x \) is the separation between two particles. 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 \( \approx R_0 \gamma \). If the springs can be considered to be independent (which is a strong 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 \( n_b N/2 \) times 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 \( V \)) is then \( \approx \kappa(n_b N/2)(R_0 \gamma)^2 \), and the shear modulus can be calculated as the second derivative of energy density with respect to \( \gamma \) as \( G \approx \kappa n_b (\phi/r^3) R_0^2 \), where we used \( N r^3 / V \approx \phi \). If the neighbors are not too far from each other, \( R_0 \approx 2r \), leading to \( G \approx \kappa n_b (\phi/r) \). This recovers the proportionality to the surface area of particles per unit volume. Further, the number of neighbors \( (n_b) \) can be estimated from the integral of the peak of the radial distribution function \([45]\); for not-too-dense systems, \( g(x_{\text{max}}) \approx 1 + b \phi \) (a Taylor expansion about infinite dilution), where \( b \) is a coefficient that depends on the interaction (e.g. \( b \approx 3 \) for hard spheres)[46]. It then follows that the first non-linear term in volume fraction is \( n_b \approx \phi^2 \), the interparticle interaction term expected in a Taylor series expansion for the Einstein-Smallwood relation gives the leading order terms. Combining these relationships leads to \( G \approx \kappa n_b (\phi/r) \approx \phi^3/r \), which is the scaling derived from our experimental measurements. Whether arriving at this result via the microscopic derivation or intuitive expansion of Einstein-Smallwood for non-interacting particles with a particle-interaction term, both lead to the relation \( R = 2.5\phi + C\phi^3/r \). 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.

3.6.2 Physical meaning of C (collaboration with Alessio Zaccone - TU Munich)

The microscopic model presented in the article include a parameter \( C \), constant of the cubic term for the reinforcement. This parameter is found different for each couple
fillers/matrix. We believe that \( C \) defines a physical length scale that can be interpreted as the maximum spacing between aggregates for which the \( \phi^3 \) term will contribute to reinforcement of the composite material. The shear modulus of the composite material is given by affine theory as \( G\kappa \phi^3 / r \), 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 \( R = G(\phi) / G(\phi = 0) - 1 \approx b\kappa\phi^3 / (rG(\phi = 0)) \), where in the last approximate equality we focus on high volume fractions. Hence we obtain the parameter \( C \) as \( C = b\kappa / G(\phi = 0) \), where we recall that \( G(\phi = 0) \) represents the shear modulus of the pure rubber with no fillers. In our microscopic model, \( \kappa \) represents the spring constant of the polymer-mediated interaction between two nanoaggregates, and has dimensions \([\text{force/length}]\), while \( G(\phi = 0) \), by definition, has dimensions \([\text{force/length}^2]\). Let us now introduce a generic length-scale \( l \), and write \( C = (b\kappa / l) / (G(\phi = 0) / l) \). Here, \( G_{loc} = b\kappa / l \) has the dimensions of an elastic modulus which measures the rigidity of nearest-neighbor nanoaggregate interaction over the length scale \( l \). If we take \( l = l^* \) such that \( G_{loc}(l^*) = G(\phi = 0) \), then clearly \( C = l^* \). Therefore, \( C \) represents the critical length scale or critical average mutual separation \( l^* \) that two nearest-neighbor nanoaggregates should be 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 Einstein-Smallwood, if the aggregates are on average farther apart than the critical separation distance \( l^* \). In our systems the average separation between two nearest-neighbor 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.

CONCLUSION

In conclusion, we studied the reinforcement of nano-filled (NBR) rubbers for which the radius of the primary particles was varied. The main achievement is that we developed a correction for Einstein-Smallwood relation to incorporate size-dependent reinforcement. Previously [25, 35], filler size has been shown to affect mechanical behavior of filled rubbers, but we here quantify and explain the physics behind the size dependence of the linear elasticity of filled rubbers. Our correction accurately models the size-dependent reinforcement of the industrial nano-filled rubbers with different polymer chemistry. In all of the systems studied, the reinforcement at volume fractions beyond the dilute regime could be rescaled in a system-independent way by taking into account a correction to the Einstein-Smallwood relation that is proportional to the third power of the volume fraction and inversely proportional to the radius of the filler aggregates. Surprisingly, the experimental results show that for both systems (NBR and
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SBR nanocomposites), this rescaling is sufficient to account for the filler-size-dependent reinforcement phenomenon; no other terms in the expansion in volume fraction are needed for the volume fraction range studied. Only a single parameter C is necessary to rescale the data once the filler (aggregate) size is known. The fact that our rescaling was obtained on one system but accurately describes the reinforcement of a separate system suggests that the rescaling presented here is unique and reveals a fundamental insight as to why small fillers are commonly and efficiently used to achieve maximal reinforcement of composite polymer materials.