

1

Introduction

The reinforcement of composite materials is far from being a simple problem [1]. Reinforced elastomers, which find application in the car tire industry, are typical and well-known examples of that. Indeed, these materials allow a physical formulation of most of the problems and offer a suggestion for a solution. Complications arise due to the many length and time scales involved and this is one of the issues which will be examined in this book.

The basic aim of filling relatively soft networks, i. e. cross-linked polymer chains, is to achieve a significant reinforcement of the mechanical properties. For this purpose, active fillers like carbon black or silica are of special practical interest as they lead to a stronger modification of the elastic properties of the rubber than adding just hard randomly dispersed particles. The additional reinforcement is essentially caused by the complex structure of the active fillers (see, e.g., [2] and references therein).

The main aim of the present work is to gain further insight into this relationship between disordered filler structure and the reinforcement of elastomers. As a filler type we have chiefly in mind carbon black, which shows “universal” (i. e. carbon-black-type-independent) structural features on different length scales, see Fig. 1.1: carbon black consists of spherical particles with a rough and energetically disordered surface [3, 4]. They form rigid aggregates of about 100 nm across with a fractal structure. Agglomeration of the aggregates on a larger scale leads to the formation of filler clusters and even a filler network at high enough carbon black concentrations. Reinforcement is thus a multiscale problem.

These universal features are reflected in corresponding universal properties of the filled system. For example, the geometry and activity of the filler surface play major roles in the polymer–filler interaction: the physical and chemical binding of polymers to the filler surfaces depends on the amount of surface disorder. Aggregate structure is expected to be dominant at intermediate length scales and agglomerate structure at large length scales. Interesting phenomena like enhanced hydrodynamic

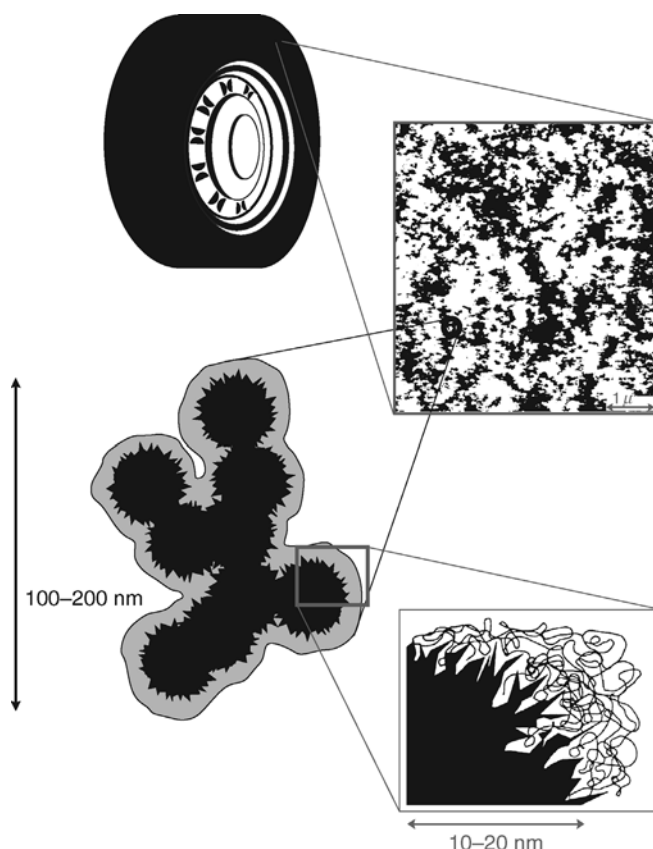


Fig. 1.1. Structural properties and scales in carbon-black-filled elastomers on different length scales.

reinforcement and the Payne effect can be attributed to the fractal nature of the filler structure. From these considerations it is clear that classical approaches to rubber elasticity are not sufficient to describe the physics of such systems. Instead, different theoretical methods have to be employed to deal with the various interactions and, consequently, reinforcing mechanisms on different length scales. Moreover, we have to indicate physical length scales as well. Considerable reinforcement can only be achieved if the length scales of the filler and the polymer matrix (Fig. 1.2) coincide.

Figure 1.2 shows the possible interplay between the length scales. The small scales defined by the structure and the interactions need to be of the same order of magnitude in order to get a significant rate of adsorption and sticking, which will contribute to the reinforcement. The larger structures, such as agglomerates

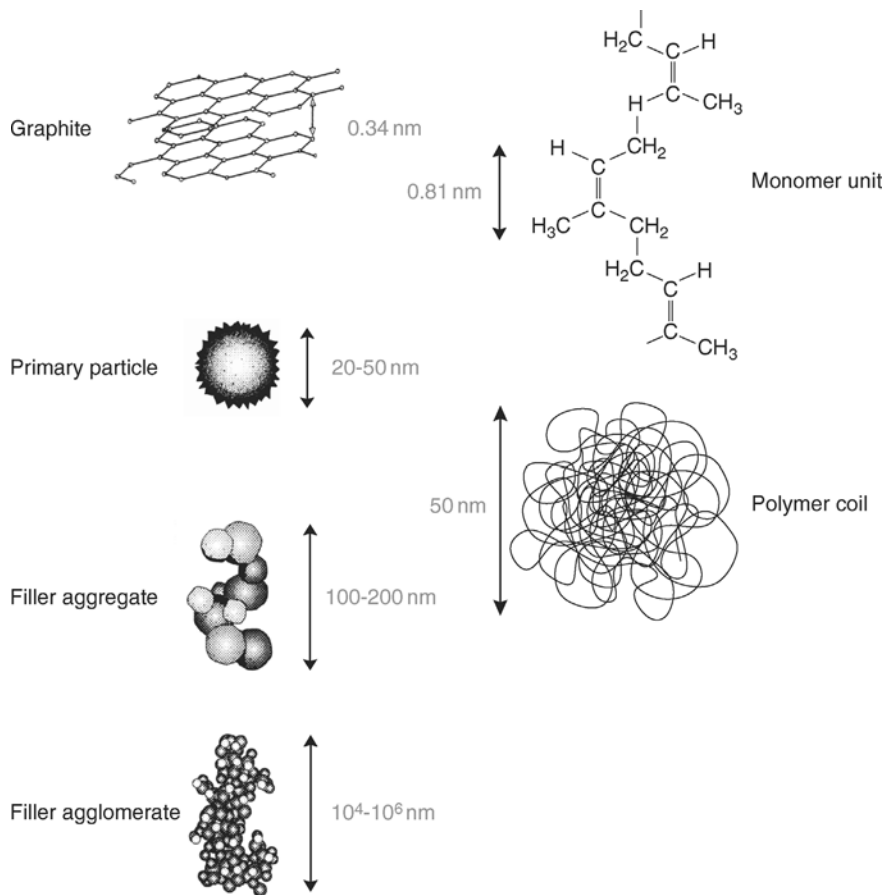


Fig. 1.2. Comparison of the different length scales for the elements. The filler particles, here carbon black, have basically carbon surfaces. These interact directly with the monomers on their length scales. However, the aggregates and agglomerates have dimensions similar to those of the polymer coils, so they can directly interact with them.

and aggregates have similar scales with typical polymer radii. Thus we can expect scale-dependent contributions to the modulus based on the interactions between rubber matrix chains and filler particles.

On yet larger scales hydrodynamic reinforcement comes into play. The basic idea goes back to Einstein and his work on the viscosity [5]. He derived an equation for the enhancement of the viscosity of solutions when spherical particles are added. This is the well-known formula

$$\eta = \eta_0(1 + 2.5\phi) , \tag{1.1}$$

where η_0 is the viscosity for the pure solution and ϕ is the volume fraction of the added spheres. The number 2.5 is purely geometrical and has its origin in the spherical nature of the added particles.

So far we have not mentioned the main contribution from the elastic matrix which comes in most cases from polymer networks, i. e. crosslinked polymer chains. The elasticity of such networks can be described on different levels (see the classical book of Treloar [6] for a basic reference). For the purpose of this book we restrict ourselves to the statistical physics description, i. e. simplified models are used which allow at least some of the molecular aspects to be taken into account. In physical terms the elastic modulus can be simply estimated: if a large number of chains become crosslinked by N_c crosslinks, each crosslink contributes with a thermal energy $k_B T$ to the elastic (free) energy. Thus the modulus in its simplest version should be of the form [7]

$$G_{\text{matrix}} \propto N_c k_B T . \quad (1.2)$$

As yet, the formation and structure of filler networks in elastomers and the mechanical response, e.g., the pronounced dynamic amplitude dependence or stress softening, of reinforced rubbers is not fully understood, though this question is of great technical interest. A deeper understanding of filler networking and reinforcement could provide a useful tool for the design, preparation and testing of high-performance elastomers, as applied in tires, seals, bearings, and other dynamically loaded elastomer components. In the past, attention has been primarily focussed on understanding the reinforcing mechanism of carbon black, the most widely used filler in the rubber industry [3, 8]. The strongly non-linear dynamic-mechanical response of carbon-black-filled rubbers, reflected primarily by the amplitude dependence of the viscoelastic complex modulus, was brought into clear focus by the extensive work of Payne [9–16]. Therefore, this effect is often referred to as the Payne effect.

As shown in Fig. 1.3 for a specific frequency and temperature, the storage modulus G' decreases from a small strain plateau value G'_0 to an apparently high amplitude plateau value G'_∞ with increasing strain amplitude. The loss modulus G'' shows a fairly pronounced peak. It can be evaluated from the tangent of the measured loss angle, $\tan \delta = G''/G'$, as depicted in Fig. 1.4. Obviously, the loss tangent shows a low plateau value at small strain amplitude, almost independent of filler concentration, and passes through a broad maximum with increasing strain.

Therefore we can expect that many different factors contribute to the modulus of a composite material. The contributions to the modulus from the different length and time scales are summarized schematically in Fig. 1.5.

The Payne effect of carbon black reinforced rubbers has also been investigated intensively by a number of different researchers [17–20]. In most cases, standard

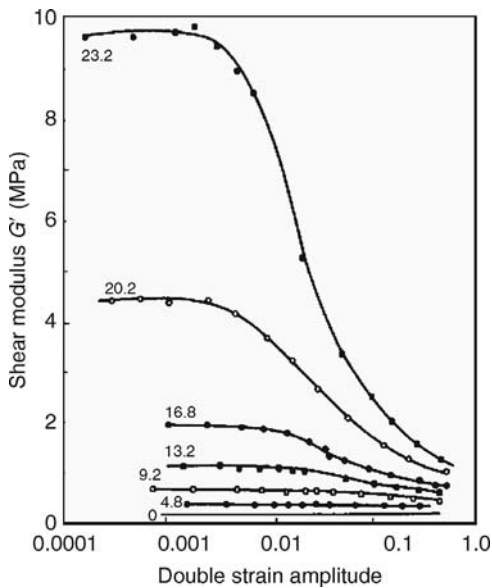


Fig. 1.3. Amplitude dependence of the storage modulus of butyl/N330 samples at various carbon black concentrations [9].

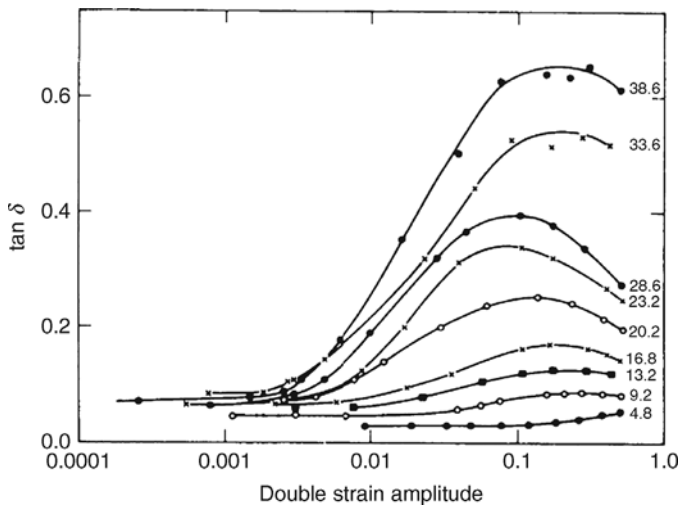


Fig. 1.4. Amplitude dependence of the loss tangent of the butyl/N330 samples shown in Fig. 1.3 at various carbon black concentrations [9].

diene rubbers that are widely used in the tire industry, such as styrene butadiene rubber (SBR), natural rubber (NR), and butadiene rubber (BR), have been employed, but carbon-black-filled bromobutyl rubbers [21–23] or functional rubbers containing tin end-modified polymers [24] have also been used. The Payne effect

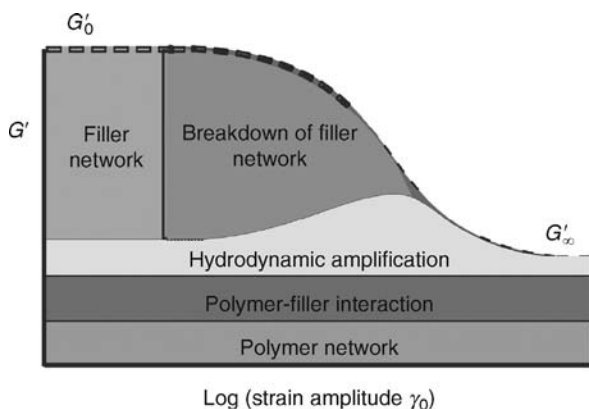


Fig. 1.5. Different contributions on different length scales build up the modulus of the material.

was described in the framework of various experimental procedures, including preconditioning-, recovery- and dynamic stress-softening studies [25]. The typically almost reversible non-linear response found for carbon black composites has also been observed for silica-filled rubbers [25–27].

The temperature dependence of the Payne effect has been studied by Payne and other researchers [9, 13, 28]. With increasing temperature an Arrhenius-like drop of the moduli is found if the deformation amplitude is kept constant. As well as this effect, the impact of filler surface characteristics on the non-linear dynamic properties of filler reinforced rubbers has been discussed in a review of Wang [28], where basic theoretical interpretations and modeling are presented. The Payne effect has also been investigated in composites containing polymeric model fillers, like microgels of different particle size and surface chemistry, which could provide more insight into the fundamental mechanisms of rubber reinforcement by colloidal fillers [29, 30].

The pronounced amplitude dependence of the complex modulus, referred to as the Payne effect, has also been observed in low-viscosity media, e.g., composites of carbon black with decane and liquid paraffin [31], carbon black suspensions in ethylene vinylacetate copolymers [32], and for clay–water suspensions [33, 34]. It was found that the storage modulus decreases with dynamic strain amplitude in a qualitative manner similar to that for carbon-black-filled rubbers. This emphasizes the role in the Payne effect of a physically bonded filler network structure, which governs the small strain dynamic properties even in absence of rubber. Further, these results indicate that the Payne effect is primarily determined by structure effects of the filler. The elastomer seems to act merely as a dispersing medium that influences the kinetics of filler aggregation, but does not have a pronounced

influence on the overall mechanical behavior of three-dimensional filler networks. However, the critical strain amplitude at which the Payne effect appears is found to be shifted to significantly smaller values if low-viscosity composites are used in place of rubber composites: This indicates a strong impact of the polymer matrix on the stability and strength of filler networks.

The strong non-linearity of the viscoelastic modulus with increasing dynamic strain amplitude has been related to a cyclic breakdown and reaggregation of filler–filler bonds [29, 35–37]. Thereby, different geometrical arrangements of particles in a particular filler network structure, resulting, e.g., from percolation as in the model of Lin and Lee [37] or kinetic cluster–cluster aggregation [29], have been considered. Nevertheless, a full micromechanical description of energy storage and dissipation in dynamically excited reinforced rubbers is still lacking.

As well as the Payne effect, which is relevant for dynamical loading of filler reinforced rubbers, the pronounced stress softening, which is characteristic of quasi-static deformations up to large strain, is of major interest for technical applications. This stress softening is often referred to as Mullins effect due to the extensive studies of Mullins and coworkers [38–40] on the phenomenon. Depending on the history of straining, e.g., the extent of previous stretching, the rubber material undergoes an almost permanent change that alters its elastic properties and increases hysteresis drastically. Most of the softening occurs in the first deformation and after a few deformation cycles the rubber approaches a steady state with a constant stress–strain behavior. The softening is usually only present at deformations that are smaller than the previous maximum. An example of (discontinuous) stress softening is shown in Fig. 1.6, where the maximum strain is increased, successively, from one uniaxial stretching cycle to the next.

The micromechanical origin of the Mullins effect is not yet fully understood [3, 17, 41]. In addition to the action of the entropy elastic polymer network, which is quite well understood on a molecular-statistical basis [42, 43], the impact of filler particles on stress–strain properties is of great importance. On the one hand the addition of hard filler particles leads to a stiffening of the rubber matrix that can be described by a hydrodynamic strain amplification factor [44–46]. On the other hand the constraints introduced into the system by filler–polymer bonds result in a decreased network entropy. Accordingly, the free energy, which equals the negative entropy times the temperature, increases linearly with the effective number of network junctions [44, 45, 47, 48]. A further effect is obtained from the formation of filler clusters or a filler network due to strong attractive filler–filler bonds [3, 17, 41, 44, 45, 47, 48].

Stress softening is supposed to be affected by different influences and mechanisms that have been discussed by a variety of authors. In particular, it has been attributed to a breakdown or slippage [49–52] and disentanglements [53] of bonds

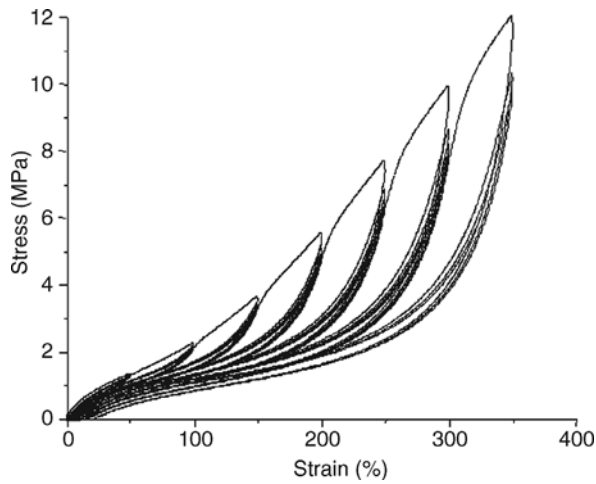


Fig. 1.6. Example of stress softening with successively increasing maximum strain after every fifth cycle for a solution SBR (S-SBR) sample filled with 50 phr carbon black.

between filler and rubber, a strain-induced crystallization–decrystallization [54,55] or a rearrangement of network chain junctions in filled systems [40]. A model of stress-induced rupture or separation of network chains from the filler surface has been derived by Govindjee and Simo [50], who developed a complete macroscopic constitutive theory on the basis of statistical mechanics. A remarkable approach has been proposed by Witten *et al.* [56], who found a scaling law for the stress–strain behavior in the first stretching cycle by modeling the breakdown of a cluster–cluster aggregation (CCA) network of filler particles. They used purely geometrical arguments by referring to the available space for the filler clusters in strained samples, leading to universal scaling exponents that involve the characteristic fractal exponents of CCA clusters. However, they did not consider, though these are evident from experimental data, effects coming from the rubber matrix or the polymer–filler interaction strength e.g., the impact of matrix crosslinking or filler surface treatment (graphitization) on stress–strain curves. The stress softening indicates that stress-induced breakdown of filler clusters takes place, where the stress on the filler clusters is transmitted by the rubber matrix.

The above interpretations of the Mullins effect of stress softening ignore the important results of Haarwood *et al.* [54,55], who showed that a plot of stress in the second extension versus the ratio between strain and prestrain of natural rubber filled with a variety of carbon blacks yields a single master curve [40, 54]. This demonstrates that stress softening is related to hydrodynamic strain amplification due to the presence of the filler. Based on this observation a micromechanical model

Cambridge University Press

978-0-521-87480-9 - Reinforcement of Polymer Nano-Composites: Theory, Experiments and Applications

T. A. Vilgis, G. Heinrich and M. Kluppel

Excerpt

[More information](#)*Introduction*

9

of stress softening has been developed invoking hydrodynamic reinforcement of the rubber matrix by rigid filler clusters that are irreversibly broken during the first deformation cycle [57, 58]. Thereby, the extended tube model of rubber elasticity, introduced in Section 5.4, has been applied [42, 43, 59, 60]. This “dynamic flocculation model” is considered in Section 10.3.

The different contributions to the elastic modulus arise from completely different physical sources. However, it is not always clear how to separate the different contributions. Roughly, we can speak of the basic contributions to the modulus of a nano-composite system. The basis for the material is the elastic matrix, which in most cases is a highly elastic polymer network. Nevertheless, the symbolic diagram shown in Fig. 1.5 will serve as a model and a guideline throughout this book.

2

Basics about polymers

2.1 Gaussian chains – heuristic introduction

This chapter introduces a convenient view of the basic physics used in the description of polymer chains that will form a network which is the elastomer matrix.

In statistical polymer theory polymer chains are very simple objects. Of course, their local chemical structure can be very rich and many properties depend on the types of monomers which are used. Nevertheless, as the chain becomes longer, the specific monomers play a smaller and smaller role. The shape of the chain depends only on the environment rather than on any of the chemical details of the monomers. Therefore the simplest model to use for the present problem is that of a random walk. Although this model is very oversimplified, most polymers can be modeled in such a way [61]. The random walk model is very instructive here. First, it serves as a simple but instructive model for general problems in the statistical physics of polymers; second, it provides the basis for the simplest model of the elasticity of networks. We will turn to the latter point shortly.

Let us study the case of random walks in more detail and on a more formal basis [62]. To be more precise we start from the set of bond vectors $\{\mathbf{b}_i\}_{i=1}^N$, which are statistically independent vectors. The probability of finding a whole set is given by

$$P\left(\{\mathbf{b}_i\}_{i=1}^N\right) = \prod_{i=1}^N p(\mathbf{b}_i), \quad (2.1)$$

where the probability $p(\mathbf{b}_i)$ is given by

$$p(\mathbf{b}_i) = \frac{1}{4\pi b^2} \delta(|\mathbf{b}_i| - b). \quad (2.2)$$

The prefactor in (2.2) comes from the assumption of isotropy and corresponds to the normalization. We are now interested in finding the distribution of the end-to-end