Towards an understanding of filled rubbers
Mermet-Guyennet, M.R.B.

Citation for published version (APA):
INTRODUCTION

1.1 THE IMPORTANCE OF UNDERSTANDING OF COMPOSITE MATERIALS

Composite materials are used in numerous daily applications. They are composed of two or more materials with significantly different properties (mechanical, thermal or optical), which are mixed in order to improve their properties. The most common composites today are concrete and filled metals or rubbers.

The filled rubbers studied in this thesis are basically a mix of hard nanoparticles (silica) and a relatively soft polymer matrix (synthetic polymer and additives). Nowadays over 10 millions of tons of carbon black and silica particles are produced each year, mainly to enhance the mechanical performance of polymers. Filled rubbers are used for tires (~70%) but also for damping devices or in architecture (to allow structures such as bridges to resist to temperatures variations), or as sealings of ball bearings (Fig. 1.1).

Figure 1.1: Two examples of the use of filled rubbers: (A) as the external layer of tires in contact with the road, and (B) as sealing of ball bearings.

To understand the properties of filled rubbers is a complex endeavor. As we will discuss, adding hard nano-fillers to a soft matrix leads to a complex aggregation phenomenon [1]. The structure of the fillers in the resulting materials directly controls its mechanical properties [2]. The aim of this thesis will be to link the micro-structure of filled rubbers to their mechanical behavior.
Chapter 1

1.2 FROM NATURAL RUBBER TO HIGH-PERFORMANCE FILLED RUBBERS

The material known today as filled rubber is a highly complex material. It has a long history starting from natural rubbers (Fig. 1.2). Natural rubber, originally from South America, can be extracted from trees such as the Hevea Brasiliensis. The mesoamerican societies already used this material for playful or religious purposes [3].

![Structural formula of natural cis-polypropene, principal ingredient of natural rubber.](image)

The story of the industrialization of the material known today starts with Charles de la Condamine, a French explorer who discovered natural rubber during the 18th century [4]. This discovery opened more than two hundred years of scientific and industrial innovations which can be summarized in four milestones.

The first of them (1768) is due to Herissant and Macquer, who succeeded in dissolving rubber in turpentine. Thanks to this process, it was finally possible to work and mold rubbers [5]. Following this in 1819, Thomas Hancock discovered that the raw material can become plastic when worked [6]. At this point, there were still many problems in dealing with the material, for example due to its behavior with temperature. At low temperatures, the material is hard and brittle but at high temperatures it is soft and sticky. This problem was solved in 1839 by Charles Goodyear (not related to the famous tire company), who discovered that when sulfur is added to the material and the resulting mixture is heated, the temperature "problem" is solved. This process, still used nowadays, is called vulcanization [7] (Fig. 1.3). The behavior of the resulting material is predominantly elastic and independent of temperature.

The last milestone is maybe the most important, dramatically increasing the range of applications of the material in daily life: the addition of carbon black (1915) [8]. Thanks to this process the properties of the resulting material could be tuned in a remarkable way (higher elasticity, better resistance to wear). During the 20th century, academic and industrial efforts focused on improving filled rubbers. While the process of
Introduction

Figure 1.3: Principle of vulcanization. The polymers are permanently linked together by sulfur bridges.

Vulcanization remained almost unchanged, synthetic rubbers were developed (Fig. 1.2) and extra additives added to the systems by a mostly "trial and error" method. A typical composition of filled rubber for a car tire is given in Table 1.1.

\[
\begin{align*}
\text{Butadiene} & : \quad \left[ \text{CH}_2 \right]_x + \left[ \text{C}_6\text{H}_5 \right]_{y} \\
\text{Styrene} & : \quad \left[ \text{CH} \right]_x \left[ \text{CH}_2 \right]_{y}
\end{align*}
\]

Figure 1.4: Synthesis of Styrene Butadiene Rubber, the polymer mostly used for filled rubbers in this thesis.

The last main milestone dates from 1992. In order to develop "green tires" (tires with a lower rolling resistance), Michelin started to replace carbon black by silica particles. Such tires lead to a lower rolling resistance, and consequently less fuel consumption [9].

1.3 A COMPLEX COMPOSITE MATERIAL

Adding fillers to a rubber dramatically changes its linear [10–15] and non-linear behavior [16–20]. In this thesis we will focus on the two most studied phenomena, the reinforcement (i.e., increase of the linear modulus by adding fillers to the matrix) and the strain softening at medium and high strains (i.e., Payne effect). We will now define these two effects.
Chapter 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Quantity (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer: Mainly synthetic rubber</td>
<td>100</td>
</tr>
<tr>
<td>Carbon black</td>
<td>35</td>
</tr>
<tr>
<td>Silica</td>
<td>35</td>
</tr>
<tr>
<td>Oil</td>
<td>20</td>
</tr>
<tr>
<td>Resin</td>
<td>4</td>
</tr>
<tr>
<td>Antioxidants</td>
<td>2</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>4</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1.5</td>
</tr>
<tr>
<td>Antioxidants</td>
<td>2</td>
</tr>
<tr>
<td>Wax</td>
<td>2</td>
</tr>
<tr>
<td>Vulcanization accelerator</td>
<td>1</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 1.1: Compounds needed to produce 200 kg of tread for a passenger-car type of tire [9].

1.3.1 Reinforcement

Figure 1.5: Representative elastic (A) and dissipative (B) behaviors of a filled rubber at low (light gray), medium (dark grey) and high (black) volume fraction of fillers.

As shown in Fig. 1.5 the modulus of filled rubbers increases with increasing filler content; this is called the reinforcement. Several models exist to account for the reinforcement [14], based on effective medium theory and mixing rules. The mixing rule (Fig. 1.6 A), considers that independently of the distribution of the fillers, the mechanical characteristics are the same. So, for instance 40 vol.% of glass beads in polymer is equivalent to 40 vol%. of glass and 60 vol% of polymers, and the modulus is a weighed
Introduction

average. The effective medium theory is more elaborate. Here the composite material is considered to be a single bead with a layer of polymer surrounding it, embedded in an effective medium (Fig.1.6B). The effective medium includes all the other beads and the polymer, and has the same characteristics as the overall material. The modulus of the material is obtained after calculations depending on the details of the model that is considered [14].

Figure 1.6: Schematic representation of the two theories introduced in this section. (A) The mixing rule: the composite is equivalent to a volume corresponding to the volume of fillers. (B) The effective medium theory: the mechanical behavior of the overall material can be found by only looking at a filler, the polymer layer surrounding it, embedded in an effective medium.

However (as we will see in Chapter 3), these models are missing one crucial ingredient which is the radius of the fillers.

1.3.2  Payne effect

In parallel to the reinforcement, the Payne effect appears. It corresponds to a strain softening (decreasing elasticity with increasing deformation, Fig. 1.5(A)) and a dissipation peak (Fig. 1.5(B)) at high volume fraction. Similar to the reinforcement, the effect becomes stronger when adding more fillers. This is a critical issue for several applications such as car tires. Indeed, the typical deformation of a car tire when rolling is about 20\%, which can correspond to a decrease of the modulus of 75\% and a large dissipation (Fig. 1.5).

The understanding of the Payne effect has remained at least as elusive as our understanding of the reinforcement. It was first characterized by Payne [17, 18]. The most commonly accepted (or less criticized) explanation involves the formation of glassy layers around the fillers and consequently of glassy bridges between them [21–23]. Under shear the deformation of these bridges lead to the strain softening associated with the Payne effect. This would imply that interfiller distances on the order of 10 nm are necessary to observe the Payne effect. It will be shown in Chapter 6 that this
Chapter 1

explanation cannot be completely satisfying since the Payne effect is observed for large particles (with radii of about 100 microns) with very large interparticle distances.

1.3.3 Chemistry and microstructure

![Figure 1.7](image)

Figure 1.7: Three-dimensional transmission electron microscopy (3D-TEM) pictures showing the aggregate structure in a given volume without a small addition of silanol group (A) and with (B)(φ=0.24). (C) Elasticity vs deformation for the filled rubbers shown in (A) and (B).

As mentioned in the previous sections, the rheology of filled rubbers is complex. The chemistry and the microstructure of these systems are unfortunately not easy to characterize but have to be elucidated for a simple reason: the three of them are interconnected [24–26].

To make this point clear, we consider two filled rubbers. The only difference between them is an small addition of silanol groups (Si-O-H) in the polymer matrix (one per polymer chain). Fig. 1.7 shows results from 3D-TEM (Transmission Electron Microscopy). A
Introduction

volume of the material is reconstructed and only the structure of the fillers appears (the polymer is not visible). We conclude from Fig. 1.7 that the microstructure of the sample seems changed. The addition of silanol groups appears to make the particle distribution more homogeneous. The mechanical behavior is also dramatically changed: on one hand the reinforcement is lowered but on the other hand the Payne effect seems to be less strong. Concerning filled rubbers, the challenge is to find a way to lower the strain softening (and, in addition, the dissipation) without lowering the modulus.

1.4 SCOPE OF THIS THESIS

Chapter 2: In this chapter we will describe the experimental techniques and the preparation protocols of the materials studied in this thesis.

Chapter 3: In this chapter we will study the filler size-dependence of the linear elasticity. We will answer the question: why are rubbers usually filled with nanosized particles? We will introduce a rescaling accounting for this size dependence at different filler size length scales.

Chapter 4: The rubbers, when subjected to shear exhibit a strong normal stresses. In this chapter we will observe that the intensity of this phenomenon increases when adding fillers. Finally we will extend the rescaling obtained in Chapter 3 and conclude that normal reinforcement and reinforcement are correlated.

Chapter 5: In this chapter we will characterize the correct overall mechanical behavior of filled rubbers. Finally we will introduce a rescaling which demonstrates that the Payne effect does not depend on the frequency.

Chapter 6: This chapter will deal with one of the hottest topic concerning filled rubbers: the Payne effect. After a brief review of the literature we will introduce new results which show that existing explanations are incomplete. We will finally use a model system to propose a possible parameter controlling the Payne effect.