Towards an understanding of filled rubbers

Mermet-Guyennet, M.R.B.

Citation for published version (APA):
Adding fillers to a polymer matrix dramatically changes its mechanical behavior. The linear modulus can increase by one or two orders of magnitude [13–15, 22, 40] and the non-linear modulus decreases at high strains, which is the so-called Payne effect [17–19, 47]. The latter has received considerable attention, but is not the only non-linear elastic effect: for polymers in general normal stresses arise at high strains [48], a non-linear effect which does not appear to have been studied in filled rubbers. Under a shear deformation most elastic solids have a tendency to feature a positive normal stress difference referred to as the Poynting effect [49–51]. However there are notable exceptions with negative normal stress such as biopolymer networks [52, 53]. Theoretically, for homogeneous rubber-like materials, a number of models have been proposed that link the normal stress with the other mechanical parameters such as the shear modulus. Perhaps the most widely used is the Mooney-Rivlin model which predicts a positive normal force that increases quadratically with the strain, with a prefactor equal to the linear shear modulus of the material [54]. This work was extended later on by Gent [55], who carefully considered the boundary conditions and concluded that for the case that pertains to most simple shear experiments, the prefactor of the normal stress is a linear combination of two Mooney-Rivlin parameters, as will be discussed in detail below. However, such models are typically constructed to account for polymer elasticity, and do not consider a potential effect due to the presence of filler particles, which are present in most if not all rubbers used in practice. The filler material by itself can be viewed as a granular material; in general one expects the well-known Reynolds dilatancy of granular materials to lead to large positive normal stresses [56]. To investigate the effect of the fillers, we will consider the effect of precipitated silica fillers in different formulations of SBR (Styrene-Butadiene) Rubber. The precipitated silica fillers are aggregates of nanometric primary silica particles, typically have a wide size distribution, and may break up during the compounding of the rubber, making the particle size ill-defined. Therefore, we also consider a model system for the filled rubber consisting of well-defined spherical particles in a crosslinked polymer gel: a polyvinyl alcohol gel crosslinked with borax and filled with micron-sized polystyrene beads. This system has the notable advantage of having controllable properties; we will notably vary the stiffness of the matrix and the radius of the fillers. We start by characterizing...
the behavior of the matrix materials for both the rubber and the PVA gel, and then focus on the filled systems.

4.1 MATERIALS AND METHODS

4.1.1 Filled rubbers and model system

We use three different types of filled rubbers. The two first types of filled rubbers are the functionalized and non-functionalized rubbers and the last is the oil-filled rubber (non-functionalized rubber with the addition of 30 phr of oil).

4.1.2 Measurements

Rheological oscillatory measurements were carried out as introduced in Chapter 2 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.

4.2 THE MOONEY RIVLIN MODEL FOR FILLED AND UNFILLED RUBBERS

4.2.1 Total strain energy of the Mooney Rivlin model

The most common model for describing the stress-strain relation of hyperelastic materials is the Mooney-Rivlin model which is much used for rubbers. The model was proposed by Mooney in [57] and then expressed in terms of invariants by Rivlin in [54]. The total strain energy density for incompressible Mooney-Rivlin materials is given by:

\[ W = C_1 (I_1 - 3) + C_2 (I_2 - 3), \]  

(4.1)

with \( C_1 \) and \( C_2 \), two material constants (the Mooney-Rivlin constants) and \( I_1 \) and \( I_2 \) are respectively the first and second invariants of the left Cauchy Green tensor.
4.2.2 Shear experiments

We carry out oscillatory shear experiments in a plate/plate geometry for which Eq. 4.1 predicts:

\[ \sigma = G \gamma_0 \]  \hspace{1cm} (4.2)
\[ G = 2(C_1 + C_2) \]  \hspace{1cm} (4.3)

With \( \sigma \) and \( G \) the stress and the shear modulus, respectively. In addition using a plate/plate geometry we measure \( N_1 - N_2 \) (with \( N_1 \) and \( N_2 \) the first and second normal stress differences respectively). For these, Eq. 4.1 predicts:

\[ N_1 - N_2 = B_N \gamma_0^2 \]  \hspace{1cm} (4.4)
\[ B_N = 2C_1 + 4C_2 \]  \hspace{1cm} (4.5)

The complete explanation about how \( N_1 - N_2 \) is determined from the normal force measured by the rheometer is given in Appendix I.

Fig. 4.1(A) and (C) shows the comparison between the measured stress, \( N_1 - N_2 \) and the predictions of the Mooney-Rivlin model. The unfilled material, unsurprisingly obeys the Mooney-Rivlin model. For the filled materials, even if \( N_1 - N_2 \) is still quadratic in strain as predicted by Eq. 4.3, the shear modulus shows strain softening at intermediate and high strains. Consequently we restrict our fit to the low-strain range to get a linear dependence of the shear modulus shown in Fig. 4.1(C).

With \( B_N \) and \( G \) measured, we can compute the Mooney-Rivlin coefficients of the samples in Fig. 4.1(A) and (C) using Eqs. 4.2 and 4.3 (Table 4.1).

<table>
<thead>
<tr>
<th>( \phi )</th>
<th>( G ) (Pa)</th>
<th>( B_N ) (Pa)</th>
<th>( C_1 ) (Pa)</th>
<th>( C_2 ) (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( 5.5 \times 10^3 )</td>
<td>( 7 \times 10^3 )</td>
<td>( 2 \times 10^3 )</td>
<td>( 7.5 \times 10^3 )</td>
</tr>
<tr>
<td>0.11</td>
<td>( 8.9 \times 10^5 )</td>
<td>( 1.1 \times 10^6 )</td>
<td>( 3.4 \times 10^5 )</td>
<td>( 1.05 \times 10^5 )</td>
</tr>
<tr>
<td>0.21</td>
<td>( 1.6 \times 10^5 )</td>
<td>( 1.9 \times 10^6 )</td>
<td>( 6.5 \times 10^5 )</td>
<td>( 1.5 \times 10^5 )</td>
</tr>
</tbody>
</table>

Table 4.1: Calculation of Mooney-Rivlin coefficients from the measured values of \( G \) and \( B_N \).

Now we can use the results from Table 4.1 and evaluate the validity of the Mooney-Rivlin model in uniaxial extension.
Figure 4.1: (A) Stress versus strain for oil-filled rubbers at zero medium and high volume fraction. The inset shows a zoom on the linear regime (i.e. low strains) and the fit from Eq. 4.2 to obtain the shear modulus versus fraction shown in (B) for each filled rubbers at each volume fraction. (C) $N_1 - N_2$ versus the square of the strain for the same samples that in (A). The line show the fits from Eq. 4.3 to obtain the prefactor $B_N$ shown in (D). (E) Prefactor $B_N$ against $G$ for each filled rubber.
Normal stress in filled rubbers under shear

4.2.3 Tensile experiments

We perform uniaxial experiments for the filled rubber 3 (they are incompressible materials). Under these conditions from Eq. 4.1 yields an engineering stress \( \sigma_{zz} = F/A \) (with \( F \) the force exerted by the tensile machine and \( A \) the initial cross section of the sample) as:

\[
\sigma_{zz} = 2(\epsilon - \epsilon^{-2})(C_1 + C_2 \epsilon^{-1}),
\]

(4.6)

with \( \epsilon \) the engineering strain. Fig. 4.2 shows a comparison of the tensile test data with the prediction of Eq. 4.4. For the unfilled material the agreement is good over the entire range of engineering strain. Again, as for shear experiments, when fillers are added, the strain softening leads to a deviation of the data from the Mooney-Rivlin model.

Figure 4.2: Fits of the engineering stress obtained from tensile testing by the Eq. 4.2 for the filled rubber 3 at zero, middle and highest volume fraction.

To summarize we can say that the Mooney-Rivlin model correctly predicts the low-strain behavior of filled rubbers both in tensile and shear experiments. To go further we can use the same model system as in Chapter 3 and extend our study to a well defined model system.

4.3 THE MODEL SYSTEM

We also investigate a model system in which filler particles are perfectly spherical, namely a polymer gel, polyvinyl alcohol (PVA), crosslinked with Borax and reinforced with micron-scale spherical polystyrene beads of different sizes. The model system, despite a very simple chemical composition and microstructure, qualitatively exhibits the same mechanical behavior as the filled rubbers.
Chapter 4

Figs. 4.3 (A) and (C) show the shear and normal stress at different volume fractions for the model system. As for the unfilled rubber, the PVA gel behaves as a Mooney-Rivlin material with again a positive and quadratic normal stress and a linear stress strain relation ($C_1 = 8 \times 10^5$ Pa and $C_2 = 1 \times 10^4$ Pa). Adding fillers, again the normal stress coefficient increases, but the modulus becomes non-linear.

Figure 4.3: (A) Stress versus strain for model system with an average radius at zero medium and high volume fraction. The inset shows a zoom on the linear regime (i.e. low strains) and the fit from Eq.4.2 to obtain the shear modulus versus fraction shown in (B) for each radius at each volume fraction. (C) $N_1 - N_2$ versus the square of the strain for the same samples that in (A). The line show the fits form Eq.4.3 to obtain the prefactor $B_N$ shown in (D).
In order to properly compare the mechanical behavior of filled rubbers and the model system, we will use the reinforcement \( R = \frac{G(\phi)}{G(\phi = 0)} - 1 \) and introduce the normal reinforcement \( R_N = \frac{B_N(\phi)}{B_N(\phi = 0)} - 1 \). For the model system, we can clearly see that the reinforcement for the shear modulus in the dilute regime varies as \( 2.5 \phi \), as is anticipated classically for this regime. The new result from these measurements is that if we plot the normal stress coefficient against the volume fraction of fillers, this also evolves as \( 2.5 \phi \), followed by a ‘concentrated’ regime in which the particles start interacting. As for the shear modulus, also here a stronger-than-linear dependence on the volume fraction is found. This leads one to suspect that the shear and normal stresses follow the same behavior when the volume fraction is increased. Plotting the normal reinforcement versus the shear reinforcement we indeed observe that they are linearly dependent on each other. Even more strikingly, the data for the filled rubber and the very different model system are on the same line, showing the universality of this dependence.

![Figure 4.4](image)

Figure 4.4: Normal reinforcement plotted versus reinforcement plotted for the filled rubbers and the model system. The grey line has a unit slope.

We can go further in this study and consider the size dependence of the reinforcement previously introduced in [58]. In this work a scaling law accounts for the size dependence of the reinforcement as:

\[
R = 2.5\phi + C\phi^3/r_{b,agg}
\]  

(4.7)

With \( r_{b,agg} \) the radius of the fillers (measured by SAXS for filled rubbers, see Appendix II) and \( C \) a scaling parameter. In order to avoid redundancy, this scaling law will not be fully explained here and we refer the curious reader to the original paper [58]. We can briefly say here that the first term of this correction corresponds to the
individual contribution of the fillers to the reinforcement. The second term is a correction accounting for the interactions between fillers, and shows explicitly the size dependence of the reinforcement. The Fig. 4.4 clearly exhibits the strong link between the reinforcement and the normal reinforcement. Consequently, the size dependence of the normal reinforcement is the same as that of the reinforcement. The scaling law found in [58] in the end is also valid for the normal stresses.

CONCLUSION

In this chapter we have studied the normal stress in filled rubbers and compared their mechanical behavior to that of a dispersion of perfectly spherical particles in a polymer gel. The normal stresses are always found to be positive and to vary with strain squared. However, even if the normal stress of these systems agrees with the predicted strain dependence given by the Mooney-Rivlin model, this is not the case for the shear stress which becomes strongly non-linear upon the addition of filler particles; the filled rubbers cannot be described by this model. It is therefore intriguing that there is a linear relation between the ‘normal reinforcement’ and the ‘shear reinforcement’ that is uncovered here.
APPENDIX I: RELATION BETWEEN $f_n$ AND $f_0$

Within a cycle of oscillation we can write the following relations, considering that the normal force is a quadratic function of the strain at the outer radius [16]:

\[
\begin{align*}
\gamma &= \gamma_0 \sin(\omega t) \\
F &= F_0 \sin^2(\omega t) \\
(N_1 - N_2)_\gamma &= \frac{F}{\pi R_p^2} (2 + \frac{d(\ln(F))}{d(\ln(\gamma))})
\end{align*}
\]  

(4.8)  
(4.9)  
(4.10)

Considering that we are studying Mooney-Rivlin materials with a quadratic $F$, this finally yields:

\[
(N_1 - N_2)|_{\gamma} = \frac{4F}{\pi R_p^2},
\]

(4.11)

with $F$ the normal force measured for a strain $\gamma(t)$ and $r$ the radius of the plate. The value returned by the rheometer can be written as:

\[
F_N = \frac{\omega}{2\pi} \int_0^T dt F_0 (\sin(\omega t))^2
\]

(4.12)

Considering that the period $T$ is $\frac{2\pi}{\omega}$ and using some trigonometry we get:

\[
F_N(\gamma_0) = \frac{F_0}{2}
\]

(4.13)

Consequently the value returned by the rheometer corresponds to the half of the normal force at a strain:

\[
(N_1 - N_2)_{\gamma_0} = \frac{8F_N}{\pi R_p^2},
\]

(4.14)

with $F_N$ the measurement returned by the rheometer during an oscillatory measurement and corresponding to a strain amplitude $\gamma_0$. And we will write the coefficient $B_N$ as:

\[
(4.15)
\]
Chapter 4

APPENDIX II: AGGREGATE SIZE MEASUREMENT

Figure 4.5: (A) SAXS spectra for the functionalized filled rubber. The inset shows the same spectra using a Krakty representation. Here, the maximum value corresponds to the aggregate radius. (B) Aggregate radius versus volume fraction for the different filled rubbers considered in this chapter.