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

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
As discussed in the previous chapters, adding fillers to a polymer matrix leads to reinforcement (see Chapter 3) but also to different non-linearities such as the Payne effect (strain softening above a few percent deformation, see Chapter 1) or local strain hardening (see Chapter 5). Filled rubbers have numerous industrial applications and in this chapter we will focus on the most important: tires. Within this context, the reinforcement benefits the durability of the filled rubbers, but the Payne effect is believed to increase the rolling resistance as the strain softening leads to an enhanced dissipation [9]. This dissipation is recognized as being responsible of 15% of the fuel consumption and consequently the tire industry seeks a way to decrease the Payne effect while maintaining the reinforcement. Unfortunately, as we will discuss, the Payne effect and the reinforcement appear to be strongly interconnected and are increasing together with increasing volume fraction of fillers.

Several studies, numerical as well as experimental, attempted to identify the microscopic origins of the non-linear elasticity of filled rubbers [17–19, 22, 24]. For sake of simplicity, here we will only discuss the most generally accepted theory that explains the reinforcement and the Payne effect. In this theory, both have the same microscopic cause: the formation of a glassy layer around the fillers. Berriot et al. [21] first observed a slowing down of the polymer dynamics around the fillers, and interpreted this as a glassy layer. This interpretation led to discussions within the filled-rubber community about the importance of such a glassy layers around fillers [25, 35, 70]. In addition, simulations linked the mechanical properties of filled rubbers with this glassy layer [22, 78, 79]. We can summarize this explanation as follows: (i) the glassy layers percolate to form glassy bridges; (ii) the percolated structure reinforces the material at low strain amplitudes; and (iii) under shear the glassy bridges are broken, which leads to Payne effect.

Several concerns can be formulated about these studies. First, the explanation only holds at high volume fractions (glassy layers need to percolate to form glassy bridges). Second, for as far as we know, there is no clear experimental proof for the existence of the glassy bridges, e.g. from DSC [35]. In addition, recent simulation works from Chen et al. [80] demonstrate that for a typical volume fraction of fillers (0-25%), there is no formation of glassy bridges but only of rubber bridges (interacting fillers). In view of
all of this, we can say that the understanding of Payne effect and its relation with the
reinforcement remains elusive.
Filled rubbers manufacturers, such as Michelin, use chemical additives to produce
better filled rubbers (less Payne effect for a given reinforcement). An example is the
functionalization (addition of silanol groups into the matrix) already introduced in this
Thesis.
In this chapter we will present some results about the control of the Payne effect
and reinforcement. We will start by evaluating the efficiency of the functionalization.
Then, using the filled PVA/Borax gel, we will present some results, introducing the
polydispersity of the fillers as an important solution.

6.1 MATERIALS AND METHODS

6.1.1 Filled rubbers and model system

The two types of filled rubbers used here are the functionalized and non-functionalized
rubbers introduced in Chapter 2 (addition of silanol groups for functionalized samples).
The model system is the Polyvinyl/Borax gel filled with 125-microns glass beads.

6.1.2 Rheological measurements

The oscillatory rheological measurements were carried out using a plate/plate geometry.
For filled rubbers the diameter of the geometry was 5 mm and the samples were disks
with a thickness of about 2.5 mm stuck on each side to avoid wall slip with a Loctite
glue. 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 sufficiently rough to avoid also
any wall slip.

6.1.3 Polydispersity measurements

The polydispersity measurements were carried out with an optical microscope Zeiss®
with a 2X objective coupled with a Pixelink® camera for imaging. The distribution of
radius was determinate using ImageJ.
Before dealing with the experimental results we need to clearly define how we will quantify the reinforcement and the Payne effect.

The reinforcement will be defined as in Chapter 3 and 4. It is the ratio of the linear modulus of the filled material and the modulus of the unfilled material (linear within the range of deformations of our experiments).

The quantification of the Payne effect is more complicated and we use the parameter Py representing the loss of reinforcement under deformation as in [81], written as:

\[
P_y(\phi) = \frac{G(\gamma_0 \to 0, \phi) - G(\gamma_0 = 0.6, \phi)}{G(\gamma_0 \to 0, \phi)}
\]  

In order to display a complete set of data we will also display the loss factor (loss modulus over storage modulus).

The Fig. 6.1 (A) and (B) compare the shear modulus and loss factor for non-functionalized and functionalized rubbers at different volume fractions. With the functionalization, the shear modulus curves are flattened. Concerning the loss factor the amplitude is not notably changed but the curve is shifted to higher strains.

We use the parameter Py to compare the drop in reinforcement under shear and the reinforcement (Fig. 6.1 (C)). Surprisingly, the data for functionalized and non-functionalized filled rubbers fall on the same curve.

To summarize we can say that the functionalization does not seem to be the optimal solution to control the Payne effect while maintaining a constant reinforcement. In addition, Fig. 6.1(C) confirms that the reinforcement and Payne effect are increasing together. Nevertheless it seems that the reinforcement increases faster than its non-linear counterpart.

To gain more insight, we need to use a model system that is easily tunable to study the mechanical behavior of the composite material.

6.3 A POSSIBLE MODEL SYSTEM FOR THE PAYNE EFFECT

The natural candidate is - again - the filled PVA Borax gel. Figs. 6.2 (A) and (B) show the shear modulus and loss factor for different volume fractions. As shown in Fig. 6.2 (C), the system is suitable only above 20% volume fraction because lower volume fractions do not exhibit a Payne effect (open symbols) For higher volume fractions (filled symbols) the reinforcement deviates from the Einstein-Smallwood equation (R=2.5\phi, i.e. the fillers are interacting) and the system features a Payne effect.
Figure 6.1: Shear modulus modulus (A) and loss factor (B) at different volume fractions for functionalized and non-functionalized rubbers. (C) Evolution of the Payne effect with the reinforcement for functionalized (gray symbols) and non-functionalized (black symbols) filled rubbers.
Figure 6.2: Rheological behavior of PVA Borax gel filled with 125-microns-radius glass beads: (A) Shear modulus for unfilled material to 45% with steps of 5%. The loss factor corresponding to these full scatters is shown in (B). (C) Reinforcement vs volume fraction for this system. The grey line corresponds to the Einstein-Smallwood equation.
Consequently the filled PVA Borax gel seems to be a good model system for the Payne effect at volume fractions above 20\%. In addition we also observe a peak of the loss factor for the highest volume fraction (i.e., when the fillers are highly interacting) consistent with the results for filled rubbers obtained in [82].

6.4 INFLUENCE OF THE FILLER POLYDISPERSITY

6.4.1 Determination of the polydispersity

The filler radius distribution is determined using optical microscopy and image processing. We define the polydispersity as the ratio of the variance and the average radius:

\[
p = \frac{\nu}{r_b},
\]

with \(\sigma\) the variance and \(r_b\) the average radius of the beads. We will use 3 different model systems with an average radius of 125 microns and polydispersity of 2, 4, and 20\%, which will be named p02, p04 and p20 respectively.

6.4.2 Results for polydisperse and monodisperse systems

The Fig. 6.4 shows the shear modulus and loss factor for these systems at 30 and 40\% volume fraction. We observe that the Payne effect is significantly reduced when
The Payne effect

Figure 6.4: Effect of the polydispersity of fillers on Payne effect and reinforcement: (A) Shear modulus and loss factor versus strain amplitude for p02, p04 and p20 (30% empty scatters, 40% full scatters). (C) Payne effect amplitude versus the reinforcement for these three systems decreasing the polydispersity (Fig. 6.4(C)). Apparently, the filler polydispersity could be the key parameter to control the Payne effect. Indeed by decreasing the polydispersity we clearly lower the Payne effect and even increase the reinforcement.

6.5 LIMITS AND FUTURE WORK

The results presented here are promising but only an opening for future work for two reasons.

- First, the definition of the Payne effect is rather arbitrary. Does any system featuring strain softening also display a Payne effect? Or is it a property of composite materials? In the literature the peak of the loss factor is used as an
extra condition of the Payne effect, however as demonstrated in [83] for filled rubbers this peak can disappear by decreasing the specific surface area of the fillers, while maintaining a comparable strain softening. Hence a good start for future research would be to define the rheological marker of the Payne effect.

- Second, the results are not understood. The reason why the reinforcement is increased by decreasing the polydispersity could perhaps be understood by including the polydispersity in the model proposed in Chapter 3. However, understanding the Payne effect appears to be more difficult. As we observed, the amplitude of the Payne effect decreases with the filler polydispersity. Including fillers modifies locally the stress field of the matrix material (Chapter 3) and we can consider that the stress field of more polydisperse systems will be more inhomogeneous. A hypothesis for future work would be to consider that these systems under shear are more subjected to rearrangement and consequently strain softening to homogenize the stress field.

CONCLUSION

In this chapter we have studied the possibility to control the Payne effect while maintaining the reinforcement using industrial as well as model systems. Using a definition of the Payne effect we found that the functionalization does not seem to be the good solution to control the Payne effect. Hence, we propose a model system featuring the same rheological behavior as filled rubbers to study the Payne effect. We determined that the filler polydispersity could be the good parameter to improve the mechanical behavior of the filled rubbers (higher reinforcement, lower Payne effect).