POLITECNICO
MILANO 1863

SCUOLA DI INGEGNERIA INDUSTRIALE
E DELL'INFORMAZIONE

EXECUTIVE SUMMARY OF THE THESIS

Time, amplitude, and frequency dependence of the Payne effect a study on silica-filled styrene-butadiene rubbers

TESI MAGISTRALE IN MATERIALS ENGINEERING AND NANOTECHNOLOGY ENGINEERING – INGEGNERIA DEI MATERIALI E DELLE NANOTECNOLOGIE

AUTHOR: JACOPO CERVI

ADVISOR: F. BRIATICO VANGOSA

ACADEMIC YEAR: 2022-2023

---

1. Introduction

Numerous applications including tires, damping devices, and belts for transmitting power utilize reinforced rubbers. These are typically vulcanized elastomers strengthened by inorganic particles like carbon black and silica. When exposed to oscillatory inputs, these materials exhibit complex behavior due to their nonlinear reaction to increasing amplitudes in oscillation. This phenomenon, known as the "Payne effect," prominently occurs within the amplitude range typical of these applications. The current study delves into the nonlinear relationship between the components of the shear dynamic modulus and the strain amplitude in torsional oscillatory experiments on SBR with varying silica contents (0, 25, 50, and 75 phr) and NBR with 60 phr of silica. An initial investigation was conducted on the shear stress responses in amplitude sweep experiments to determine the presence and relevance of higher harmonics, utilizing Fourier Transform coefficients. This provided a well-posed basis for the application of the linear analysis which adopts the storage and loss components of the dynamic modulus in the results interpretation. A key aspect of this master's thesis is investigating the reversibility of structural changes induced by the Payne effect, which remains not fully understood in literature. The study also examines how the dynamic modulus's nonlinear dependency on amplitude is influenced by factors like filler content and applied frequency. In particular, the research aims to ascertain the separability of frequency and amplitude variables to simplify the analysis of this complex phenomenon.

2. Theoretical Background

The Payne effect takes its name from the first scientist who brought to the attention the softening shown by filled rubber under increasing strain amplitudes in 1962 [1]. This softening occurs as a reduction of the storage component of the dynamic modulus just after a linear region called G'_0 in shear conditions. Instead the loss component, after the linear region at low amplitudes (G''_0), shows a maximum and then it decreases toward lower values than G''_0. Despite a plethora of studies has been conducted on this phenomenon because of its central role in many fields, its structural interpretation is not completely understood yet. It's important to point out that the definition of the dynamic modulus comes from the application of a linear analysis, which leads to the constraint that the response to sinusoidal inputs must remain sinusoidal. Many nonlinear systems show that their output is not a simple sinusoidal function and so the response could be expressed as a linear combination of sinusoidal functions (Fourier series) where in case of a linear system only one harmonic is present. In order to support the use of the storage and loss moduli, the analysis of the higher harmonics must be done. The reversible nature of the Payne effect has been studied by Sternstein at all. in 2000 [2] who has found that filled rubber would recover the G'_0 in time after having applied preconditioning at high amplitudes and an increasing strain amplitude test. Therefore, it seems that the softening of G' induced by the Payne effect is reversible in nature. The preconditioning has crucial implications though because it is often employed in order to eliminate any irreversible effect (sometimes associated to Mullins effect). In fact some works [3] see a decrease of the storage modulus applying a series of subsequent amplitude sweeps to virgin specimens which is classified as irreversible. The present work would investigate first the identification of the effects caused by amplitude sweep on virgin specimens, second the nature of these changes to define if they are reversible or not.

Another peculiar characteristic observed in filled rubber under increasing amplitudes by Sternstein at all. in 2000 [2] and Li at all. in 2017 [5] is that varying the frequency used the functional dependence of the components of the dynamic modulus on the amplitude. In other words they have seen that, for a broad range of frequencies (0,004 – 10 Hz), the amplitude and the frequency variables of the moduli could be separated as mathematically shown in the following equation ((2.1):

$$\begin{cases} G'(\gamma_0,\omega) = G'_0(\omega) f(\gamma_0) \\ G''(\gamma_0,\omega) = G''_0(\omega) g(\gamma_0) \end{cases} \quad (2.1)$$

in this work the separability has been investigated normalizing each modulus component by its own low amplitude modulus (G'_0 and G''_0) as done by Li at all in 2017 [5].

3. Materials and methods

The analysis into this thesis is performed on the following materials: styrene-butadiene rubber (SBR) filled by 0, 25, 50, and 75 phr (parts of filler per hundred parts of rubber by weight) silica particles, indicated as SBR 0, SBR 25, SBR 50 and SBR 75, respectively and an acrylonitrile-butadiene rubber (NBR) with 60 phr of silica (NBR60). The four batches of uncured SBR are produced from E-SBR 1500 (containing 23% styrene) by Versalis using silica Zeosil 1165 MP di Solvay. The different mixtures are then cured in a press under 10 MPa at 170 °C for 10 minutes to produce rubber sheets from which rectangular samples with dimensions 34x9x3 mm^3 were die cut. The sizes are suggested by the work of L. Di Giosia on similar materials [5]. The curing cycle NBR with 60 phr of silica cannot be disclosed due to confidentiality agreement. The NBR rectangular specimens have similar dimensions 34x9x2 mm^3 die cut from an initial rubber sheet.

The oscillatory experiments are performed using the Anton Paar MCR502 Rheometer in strain control with a torsional setup.

The tests are mainly divided in three typologies:

1. Amplitude sweep test which consists in a stepwise logarithmically increasing strain amplitude (0,01 – 30 %), performed at different constant frequencies (0,1 – 1 – 5 – 10 – 20 rad/s). The test has been conducted on unstrained specimens to study the reinforcing effect with respect to the silica content on the shear dynamic moduli. Additionally, comparing the results coming from different frequencies the test helps to verify if the frequency-insensitive feature of the Payne effect holds for this system.
2. A sequence of amplitude sweep tests which incorporate three increasing strain amplitude sweeps, the first applied to the unstrained material, and labeled as "#0" to highlight that the specimen did not undergo previous tests, the second and the third, labelled as #1 and #2, are applied after having waited the same rest period of time. This test is used to investigate and determine how G' and G'' dependence on the shear strain amplitude would

be affected by repeating application of high shear amplitudes.

3. At the end of the previous test a third type of test is performed, in which a constant low strain amplitude (0,01%) is applied for a long time, spanning several time decades ($10^3 - 10^4 - 10^5$ s). This analysis has the goal to understand if the nature of the structural changes induced by the amplitude sweeps are reversible or irreversible.

The last two tests were carried out at different frequencies (5 – 10 – 20 rad/s).

4. Experimental results

4.1. Linearity of the oscillatory response

To assess the degree of non-linearity due to the large shear strain amplitude applied to the sample, the FT-rheology was applied. In this technique the stress response is described as a linear combination of sinusoidal functions. Considering the ratio between the intensity of the third harmonic and the first one (I(3ω)/I(1ω)) it's possible to verify the higher harmonics significance in the shear strain amplitude range considered here. Results of (I(3ω)/I(1ω)) are obtained (Figure 1) performing a single amplitude sweep test (for SBR 0, 25, 50, 75 phr) and processing the data about the stress responses.

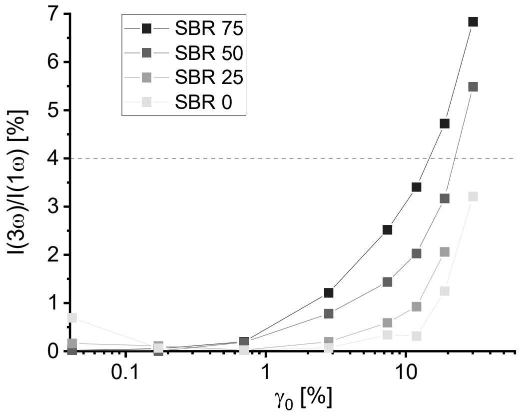

Figure 4.1. Third to firsts harmonic intensity ratio, (I(3ω)/I(1ω)), vs shear strain amplitude for filled SBR with different amount of silica.

In literature [4] it is said that the ratio limit to neglect higher harmonics is 4% as the dashed line show in Figure 4.1. Although from the graph it's reported that this limit is exceeded at high amplitude, the values are still lower than 10%. We consider this value low enough to neglect higher harmonics supporting in this work, and carry on the investigation based on the linear viscoelasticity theory.

4.2. Filler effect

The results from the single amplitude sweep test on each material are shown in Figure 4.2 in terms of $G'(\gamma_0)$ (a) and $G''(\gamma_0)$ (b) functions.

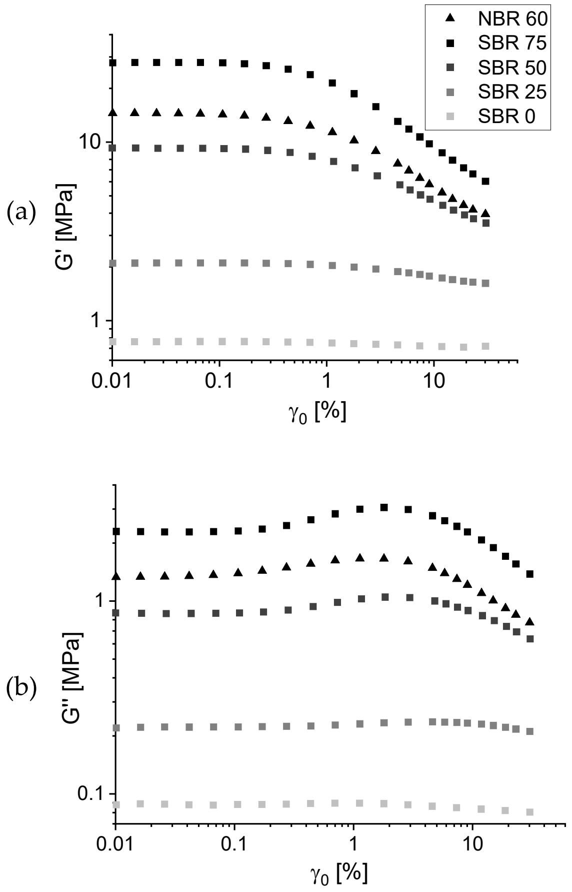

Figure 4.2. (a) G' and (b) G'' vs. γ_0 for filled SBR and NBR 60

The data show the typical trend of Payne effect and also that the material properties are enhanced the higher amount of silica is dispersed into the rubber matrix, in line with literature [1].

4.3. Shear strain amplitude effects

The series of three consecutive amplitude sweeps (sweep #0-#1-#2) separated by a rest time is performed on all the materials at 20 rad/s, the obtained results are shown in Figure 4.3.

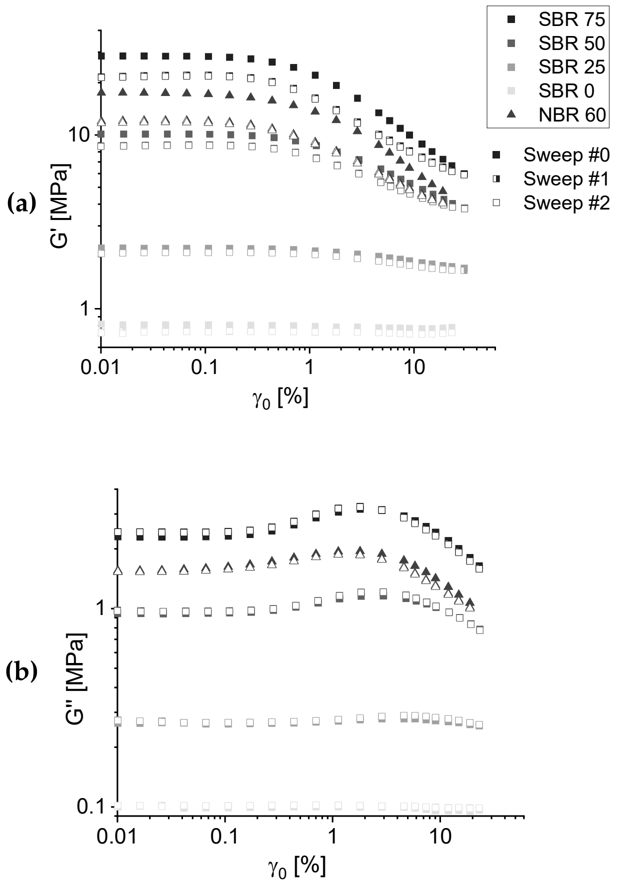

Figure 4.3. (a) G' and (b) G'' vs. γ_0 at 20 rad/s for SBR materials and NBR 60; the three sweeps are represented as full symbols for sweep #0, half-full symbol for sweep #1 and empty for sweep #2

From figure 4.3, for each material the G′ curves of sweeps #1 and #2 overlap, but they are lower than the sweep from virgin specimen #0. Therefore, it seems that just virgin materials are softened by the amplitude sweep test and then the materials do not change anymore. Although, the different sweeps curves of G′′ show significantly smaller effects than G′, the amplitude sweep test causes an increase of the loss modulus in addition to the G′ reduction. Another difference is that sweep #1 and #2 curves seem to display a second plateau at high amplitude region, which is not present in the #0 one.

Focusing on the low amplitude moduli, the ratio between the components of the complex modulus from tests #2 and #1 shown in Figure 4.4 demonstrates that the sweeps #1 and #2 overlap.

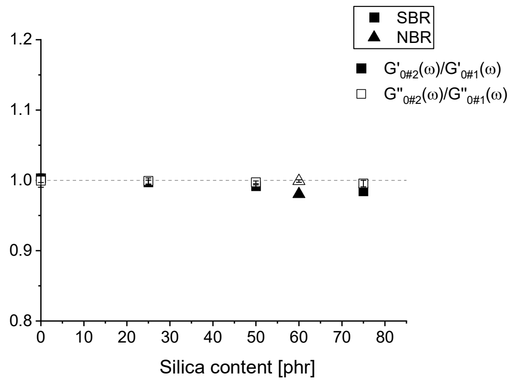

Figure 4.4. Ratio between the components of the complex modulus from tests #2 and #1 vs. filler content

From these results, it is possible to conclude that the possible structural changes of the material induced by the intermediate amplitude sweep #1 have not influenced the recovery kinetics. This is because in the two equal rest times, the material recovers the same portion of the modulus at low amplitudes.

4.4. Time effect – initial structure recovery

In literature [2] it’s been seen that the low amplitude storage modulus, after the Payne effect, recovers with a certain kinetic the initial starting value. Despite this, literature also reports that the softening observed in a series of amplitude sweeps is in general associated to the irreversible effect of Mullins effect. In the present paragraph, the constant amplitude and frequency test performed subsequently the three previous sweeps is aimed at monitoring the low amplitude modulus evolution in time, focusing only on the storage component, $G'_{0\#3}(t)$, because the loss component variation are very small. To assess this, the monitoring time of the materials spans several decades of seconds. Comparing the results with the low amplitude modulus of the virgin specimen ($G'_{0\#0}$) is useful to verify the reversible nature of the amplitude induced softening. To compactly report the results for each material, the ratio between the recovering storage modulus and the virgin storage modulus is calculated ($G'_{0\#3}(t)/G'_{0\#0}$) and shown in Figure 4.5.

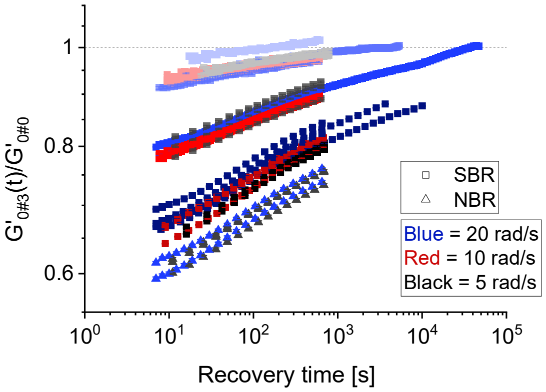

Figure 4.5. $G'_{0\#3}(t)/G'_{0\#0}$ time dependence in a double logarithmic plot

Figure 4.5 shows that the materials are able to recover their pristine low amplitude storage modulus. This suggests that the structural changes induced by the Payne effect are reversible in nature for these silica filled rubbers. However the recovery kinetic remains slow, so sufficient amount of time has to pass to recover completely the property loss.

The attention has been focused just on the storage modulus for the sake of synthesis and because the effects of amplitude are much less significant on the loss modulus.

4.5. Frequency effects

The frequency and amplitude separability has been assessed by performing the single amplitude sweep test for different frequencies (0,1 – 1 – 5 – 10 – 20 rad/s). In order to quickly verify this, the normalization of the curves at different frequencies as described in equation has been carried out.

$$\begin{cases} \dfrac{G'(\gamma_0,\omega)}{G'_0(\omega)} = f(\gamma_0) \\ \dfrac{G''(\gamma_0,\omega)}{G''_0(\omega)} = g(\gamma_0) \end{cases} \qquad (4.1.)$$

The superposition of the curves would demonstrate that the separability of the variables holds, so the frequency does not affect the amplitude dependence of the moduli. The normalized data taken from the amplitude sweeps at different frequencies are shown in Figure 4.6.

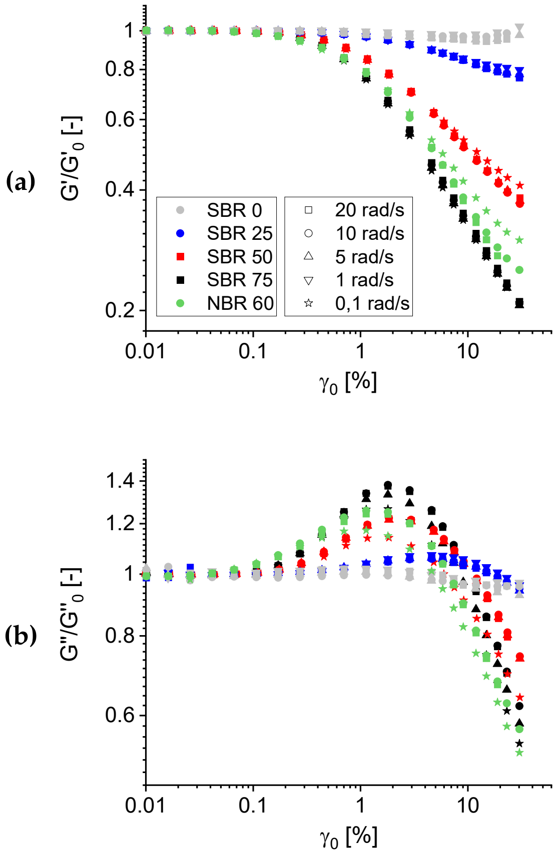

Figure 4.6. The normalized shear (a) storage and (b) loss moduli for SBR 0, 25, 50 and 75 and NBR 60 as a function of the shear strain amplitude

Observing the results, it becomes clear that the separation of frequency and amplitude variables seems valid especially at lower shear strain amplitudes. Additionally, it can be observed that at lower frequencies (0,1-1 rad/s), the superposition is less effective, indicating an interplay between shear strain amplitude and angular frequency. This is especially evident for the dissipative component of complex modulus. SBR 50 and NBR 60 materials most prominently display the observed behavior, with their low-frequency curves showing distinct deviations from other frequencies: specifically, a higher storage modulus ratio at larger shear strain amplitudes and a notably smaller peak in the loss modulus ratio. The increased storage modulus ratio at higher amplitudes could be due to the emergence of higher harmonics, which impact the separability of frequency and amplitude. Analysis of the loss modulus data indicates that at lower frequencies, there is lower dissipation compared to higher frequencies. This could be attributed to partial recovery during tests, but this factor is not as impactful for the loss modulus. Alternatively, a more plausible explanation is that materials with intermediate silica content undergo different deformation mechanisms at lower frequencies, possibly involving reduced molecular desorption from the silica particles' surface, given the extended time available for molecules to adjust to the applied shear strains.

5. Conclusions

The main conclusions of this investigation are the following:

- The higher harmonics presence could be neglected for this system because their intensity relative to that of the first one is less than 8% respect for shear strain amplitudes lower than 30%. This supports the use of linear viscoelastic theory to define materials properties in terms of G' and G'';
- The single amplitude sweeps test's results are in accordance with literature [1] in terms of Payne effect and reinforcing effect induced by the silica content, the second plateau at high amplitudes is a typical characteristic of Payne effect which is not visible in the shear strain amplitude range selected;
- If shear strain amplitude sweeps are repeated on the same sample, waiting the same set time between on test and the subsequent, only the first application of large strains causes a softening of the material, while the G' and G'' curve vs. strain amplitude is the same for all the other sweeps. Compared to the relevant curves for the unstrained material, G' curve show a lower value at low amplitude and a plateau value at high amplitudes, while G'' curve shows less pronounced increase at low amplitudes;
- The difference of G'_0 between the shear strain amplitude curves for the unstrained material and the strained one is reversible for all the considered materials: by exploiting a small strain oscillatory experiment, the kinetics of G'_0 recovery could be followed from the end of high shear amplitude application for long time, highlighting that all materials recovered the unstrained G'_0 value. The time to recover the initial value is longer for higher filler amounts. This makes the common association of Payne effect with the irreversible Mullins effect [5] questionable;
- The frequency and shear strain amplitude separability holds for higher frequencies (5 – 10 – 20 rad/s), but normalized curves at 0.1 rad/s, do not overlap with others probably due to a difference in deformation mechanism in terms limited rubber molecules desorption from the silica particles, related to a longer time available for re-absorption available when shear strain application frequency is low.

References

[1] A. R. Payne, "The dynamic properties of carbon black-loaded natural rubber vulcanizates. Part I," *Journal of Applied Polymer Science,* vol. 6, no. 19, pp. 57-63, 1962.

[2] L. Chazeau, J. D. Brown, L. C. Yanko and S. S. Sternstein, "Modulus Recovery Kinetics and Other Insights Into the Payne Effect for Filled Elastomers," Center for Composite Materials and Structures Rensselaer Polytechnic Institute, Troy, New York, 2000.

[3] M. Rendek and A. Lion, "Strain induced transient effects of filler reinforced elastomers with respect to the Payne Effect: expirements and constitutive modelling," *ZAMM,* vol. 90, no. 5, pp. 436-458, 2010.

[4] S. Li, Y. Mi and X. Wang, "Superposed nonlinear rheological behavior in filled elastomers," *Journal of Rheology,* vol. 61, no. 3, pp. 409-425, 2017.

[5] L. Di Giosa, "Dynamic Mechanical Analysis in torsion on silica-filled styrene-butadiene rubber," 2022.