Influence of the mechanical stress and the filler content on the hydrostatic compression behaviour of natural rubber

Jan Zimmermann, Markus Stommel
Chair of Polymer Materials, Saarland University, Saarbrücken, Germany
j.zimmermann@mx.uni-saarland.de

Abstract. The behaviour of natural rubber (NR) compounds under mechanical stress is often reported in literature. An important and widely discussed effect that occurs is the Mullins effect. During the first loading cycles in a tensile test for example, a stress-softening effect is observed. This and other effects on the mechanical behaviour are investigated for different rubber materials with and without different types of fillers and filler contents. Besides, the hydrostatic compression behaviour is affected by the type and content of filler as well, which is shown for an NR with and without waxes and different contents of carbon black (CB) in this contribution. In contrast to the Mullins effect, there is no dependence of the number of loading cycles on the volumetric behaviour determined in hydrostatic compression tests. Furthermore, the influence of the previous stress-softening due to mechanical stress on the compression behaviour is elaborated. Cyclic uniaxial tensile tests are performed to realize the stress-softening in the rubber materials. The subsequent compression tests are compared to compression tests without any pre-stretching to determine the influence of previous mechanical loading on the compression behaviour of natural rubber with different filler contents.

1. Introduction
The dimensioning of rubber components by finite element (FE) simulations is generally applied. In common FE tools several material models are implemented to represent the hyperelastic material behaviour of rubber via a formulation of the strain energy function, for example Mooney [1], Ogden [2], Kilian [3] or Heinrich [4]. In general, the material behaviour and therewith the strain energy function is split into a volume preserving (deviatoric) and a volume changing (volumetric) part. Both parts can be expressed dependent on the invariants $I_i$ of the left Cauchy-Green strain tensor, in which the first and second invariant describe the deviatoric, the third one the volumetric part of the respective function. The derivation of these functions results in an expression for the stresses. The approach according to Kilian [3] is stated in the equation (1) as well as the respective Cauchy stress:

$$ W = \mu \left[ -\left( J_{el}^2 - 3 \right) \left( \ln(1-\eta) + \eta \right) - 2/3 \alpha \left( \frac{I_3 - 3}{2} \right)^{3/2} \right] + \frac{K}{2} \left( \frac{J_{el}^2 - 1}{2} - \ln J_{el} \right) + W_{dev}(I_1, I_2) + W_{vol}(I_3 = J_{el}) $$

(1)
with
\[ \eta = \frac{i-3}{\sqrt{\lambda_m^2 - 3}} \]
(2)
\[ \bar{I} = (1 - \beta)I_1 + \beta I_2 \]
(3)
and
\[ I_1 = \bar{I}_1^2 + \bar{I}_2^2 + \bar{I}_3^2 \]
(4)
\[ I_2 = \bar{I}_1^2 \bar{I}_2^2 + \bar{I}_1^2 \bar{I}_3^2 + \bar{I}_2^2 \bar{I}_3^2 \]
(5)
\[ \bar{J}_i = J^{-1/3} \lambda_i \]
(6)
\[ J_{el} = \text{det} F = \lambda_1^2 \lambda_2^2 \lambda_3^2 \]
(7)
\[ \sigma = \frac{1}{J} B : \frac{\partial W}{\partial B} = S - p I \]
(8)

\( \mu \) = initial shear modulus; \( \lambda_m \) = locking stretch; \( \alpha \) = global interaction parameter; \( \beta \) = linear mixture parameter; \( I_i \) = invariants of the left Cauchy-Green strain tensor \( B \); \( J_{el} \) = elastic volume strain; \( K \) = bulk modulus; \( \lambda_i \) = (deviatoric) stretch; \( F \) = deformation gradient; \( \sigma \) = Cauchy stress tensor.

The required material parameters for the deviatoric part are determined by one or a combination of different mechanical tests like uniaxial tensile or simple shear testing. The assumption of nearly incompressibility and therefore the precondition of the bulk modulus \( K \) exceeding the material’s shear modulus \( \mu \) by several orders of magnitude is commonly accepted and applied [5]. Concerning simple loading conditions of a rubber part, a material model calibration based on these tests and the precondition \( K/\mu >> 1 \) provides a sufficient result quality of FE simulations. Hereby, \( K \) is set based on experience in common practice, since its impact on the FE result is nearly negligible [6]. The influence of the volumetric part and therefore its material parameter, the bulk modulus, increases significantly when rubber components are (partially) exposed to hydrostatic pressure, like for highly confined rubber components where a change in shape of the rubber is constrained [6]. Several approaches were published with the aim to further improve the simulation quality with respect to the volumetric part of the strain energy function of which some are summarized by Hartmann and Neff [7]. The material parameter related to the volumetric part, the bulk modulus \( K \) is defined in equation (9):
\[ K = \frac{\partial p}{\partial (\Delta V / V_0)} \]
(9)
\( p \) = pressure; \( \Delta V \) = volume reduction; \( V_0 \) = initial volume.

The mechanical behaviour and therewith the material parameters like shear modulus is highly affected by the rubber’s composition or more precisely by the type and content of its fillers. Carbon black (CB) as active filler increases the material’s stiffness as well as its wear hardness for example. Ageing inhibition and plasticizer are added to improve the component’s performance. The material modelling and simulation are based on versatile mechanical tests of rubber compounds to determine their behaviour under different loading conditions. During the first loading cycles a stress-softening occurs which is known as Mullins effect [8]. Due to partially irreversible processes like breakage of filler agglomerates the stress softening as well as a permanent set within the first four to ten repetitions of a quasi-static loading and unloading is observed. Since the first description of this effect by Mullins its cause or the influence of the type of rubber and filler are investigated in many publications and are still widely discussed. [8-14]

In contrast to effects related to the mechanical loading condition and its history the hydrostatic compression behaviour in general and the influence of fillers on this in particular are rarely or not at all reported in literature to the author’s knowledge. In [5] and [15] the dependence of relative volume reduction on hydrostatic pressure is described for a filled, technical natural rubber (NR) compound which shows the same characteristics as depicted in Figure 1. The bulk modulus corresponds to the
ratio of $\Delta p$ and $\Delta V/V_0$ and reaches a nearly constant value when the volume strain exceeds a certain level.

In this contribution the volumetric behaviour for a technical NR compound is determined. Further hydrostatic compression tests are conducted to evaluate the influence of decreasing carbon black content as well as the impact of omitted additives like plasticisers or antioxidants. The compounds are exposed to four loading unloading cycles to determine a possible effect on the volumetric behaviour. Based on these test results the evolution of the ratio $K/\mu$ in dependence of the CB content is analysed, which represents a crucial parameter for achieving an adequate simulation result quality. Due to the stress softening effect occurring during the first loading cycles, the influence of uniaxial pre-stretching on the hydrostatic compression behaviour is investigated.

![Figure 1. Relation of hydrostatic pressure on relative volume reduction [6].](image)

2. Experiments

Cylindrical samples were prepared with a technical NR compound used for tread surfaces in automotive industry (I) which is shown in Table 1. Based on this compound the CB content in II to IV is reduced by one third each, whereas in V to VIII plasticiser and ageing inhibition, columns 4 to 7 in Table 1, is left out though they show the same CB content as I to IV, respectively. Compound VIII represents an unfilled NR. I-IV are named “with waxes”, V-VIII “without waxes”. For each compound three hydrostatic compression tests are conducted with transfer moulded, cylindrical specimens (diameter: 18 mm, length: 100 mm). To extract and eliminate the system’s response a reference measure is conducted using a steel specimen instead of rubber with the same volume as the samples. A more detailed description of the testing procedure can be found in [6].

The mean value and standard deviation of three compression tests results for each compound are evaluated. The first of the three specimens is exposed to four loading cycles to detect a possible influence of previous loading steps during compression tests. Another set of hydrostatic compression tests is conducted to investigate the influence of stress-softening due to uniaxial tension on the resulting volumetric behaviour under hydrostatic pressure. Therefore rubber plates of each compound were prepared and subjected to four cyclic uniaxial loadings. In a second step these plates were cut into stripes of the same volume as the cylindrical samples to carry out hydrostatic compression tests. Furthermore the stress strain behaviour during uniaxial loading is recorded and analysed to obtain a
value for the initial shear modulus for each compound. Therewith the evolution of $K/\mu$ depending on the filler content can be gained.

Table 1. Composition of investigated rubber compounds.

| Ingredient            | I [phr] | II | III | IV | V [phr] | VI | VII | VIII |
|-----------------------|---------|----|-----|----|---------|----|-----|------|
| NR                    | 100     |    |     |    |         |    |     |      |
| carbon black N115     | 50      | 33 | 17  | -  | 50      | 33 | 17  | -    |
| zinc oxide            | 4       |    |     |    |         |    |     |      |
| Vulcanox 4020 (6PPD)  | 2       |    |     |    |         |    |     |      |
| Vulcanox HS (TMQ)     | 2       |    |     |    |         |    |     |      |
| Antilux 654           | 1,5     |    |     |    |         |    |     |      |
| Vivatec 500           | 4       |    |     |    |         |    |     |      |
| stearic acid          |         |    |     |    | 2       |    |     |      |
| sulphur               |         |    |     |    | 1,75    |    |     |      |
| Vulkacit CZ (CBS)     |         |    |     |    | 1,75    |    |     |      |

3. Results and discussion

In this chapter the results of the conducted experiments are presented and interpreted. The effects occurring are compared to findings published so far. First, results of simple hydrostatic compression test are presented, followed by those of pre-stretched compression tests. Afterwards, the impact on FE simulations is discussed briefly. Furthermore, the dependence of the number of loading cycles on the volumetric behaviour is determined.

3.1. Hydrostatic compression tests

The influence of CB content as the main reinforcing additive in NR compounds on the volumetric behaviour is determined by hydrostatic compression tests. In Figure 2 the results for compound I to IV (s. Table 1) are presented, the standard deviation recorded for the different tests is less than 3%. For lower volume strain values the pressure response shows a slight curvature where the gradient of the curve and therefore the bulk modulus increases about one decade. The response obtained after exceeding a pressure level of about 10 bar is nearly linear and represented by a constant bulk modulus. Since there is some gas in the system, the very first volume reduction compresses this and does not affect a rise in pressure, which is considered in the evaluation and the resulting curves are shifted horizontally towards the origin. This characteristic curvature may be caused by atomic-scale free volume holes, which are for example studied in (16, 17). When volume inside the chamber is reduced, at the beginning, the free volume impedes a soaring of pressure until it is occupied by water or the holes are nearly closed. The lower resistance against compression leads to the curvature at small volume strain.

An increasing CB content effects a decrease in the number of free volume holes [16] and therefore reduces the range of volume strain with a non-linear pressure response and lower bulk modulus (s. Table 2). Furthermore, by increasing the CB content, the gradient, and therefore the bulk modulus increase as well. The pressure response of compound IV deviates from the other curves, a significant increase in pressure is first detected for volume strain exceeding 0.01. This may be due to trapped air inside the specimen during the curing process as well as a larger number and size of free volume holes, since sulphur leads to these both effects and this compound does not possess any carbon black which reduces this number. A similar result is obtained for compounds without plasticiser and ageing inhibition, V to VIII, which show a curvature for lower pressure values followed by a linear progression for higher values (s. Figure 3).
Figure 2. Influence of CB content on hydrostatic compression behaviour (I-IV).

Figure 3. Influence of CB content on hydrostatic compression behaviour (V-VIII).

The resulting bulk moduli for the linear range of the pressure response are summarized in Table 2. A reduction of the CB content leads to a decrease in bulk modulus for both NR with and without waxes of approximately 20 %). Furthermore, compounds without waxes show about 4 % higher bulk moduli compared to those with waxes for the same CB content, respectively, which leads to the conclusion that the bulk stiffness is increased for those rubbers. This effect is due to the higher volume fraction occupied by CB compared to technical NR, since the bulk modulus of carbon black exceeds those of rubber and waxes by an order of magnitude (K_{CB} \approx 30 \text{ GPa}). On the other hand waxes reduce
the bulk modulus of NR which can be seen by comparing both compounds without any CB. This effect may be reasoned in the higher compressibility of waxes compared to NR as well as in the filler-rubber network which is built during in the curing process. A more detailed determination of the observed effects and its cause is topic of current research.

![Figure 4. Influence of loading cycles (II and III).](image)

3.2. Hydrostatic compression tests with previous uniaxial tensile loading

![Figure 5. Uniaxial tensile tests - influence of CB content (left), stress-softening effect (right).](image)

Besides the initial hydrostatic compression behaviour as shown in Figure 2 and Figure 3 the effect of further loading cycles is determined. In Figure 4 the resulting pressure over volume reduction of the first and fourth cycle is depicted for compounds II and III representing a technical rubber compound with 33 phr CB or 17 phr CB, respectively. The corresponding curves still possess a similar progression whereas the hydrostatic pressure with respect to volume strain, and therefore the bulk modulus, shows an increase from the first to the last loading cycle of about 10 % for technical NR compounds with 0 phr or 17 phr CB, respectively. This phenomenon is caused by free volume holes as well. During each compression phase, free volume is compressed and partially occupied by penetrating water. This will not be removed completely before the following loading step, so that the
number and size of free volume holes decreases which reflects in the slightly higher increase in curvature at low volume strain with on-going loading. Furthermore, an offset in volume, that is necessary to arouse an increase in pressure, is detected, which decreases with the number of loading cycles. A possible breakage of filler cluster may also contribute to the observed behaviour. Besides, due to the occupied volume the increase in bulk modulus can be detected. The compounds with higher CB content show a slightly lower increase in K of about 6 %, since the number of free volume holes reduces with higher CB content [16]. A continuing testing after the first four loading cycles leads to a steady state in the dependence of volume strain and hydrostatic pressure.

The compound without waxes show the same behaviour, there is an increase in bulk stiffness detected during the very first loading cycles. In future research swelling experiments are to be conducted to determine the absorption of each specimen and more precisely each compound. A comparison of these results to the volume reduction found during the cyclic compression tests is to be drawn to confirm the assumption of free volume holes influencing the hydrostatic behaviour.

Figure 6. Influence of filler content and stress-softening on shear modulus.

Since the stress-softening effect significantly influences the mechanical behaviour and directly the shear modulus, a possible effect of uniaxial pre-stretching on hydrostatic compression is investigated. Besides, for modelling the material behaviour in FE analysis the shear modulus as a material parameter is required. Therefore uniaxial tensile tests are conducted and the stress strain response is extracted. Figure 5 shows exemplary decreasing stress responses due to a decreasing CB content (I-IV) as well as the stress-softening effect for compound III. The evolution of μ with respect to filler content as well as a comparison of the resulting shear modulus with and without stress-softening is depicted in Figure 5. The stress-softening effect occurs even for compounds without any CB, however the gap between μ with and without softening increases with CB content. Moreover, an increasing CB content causes an increasing shear modulus for both, compounds with and without waxes, respectively. Waxes soften the material and therefore lead to a lower μ (I-IV) compared to compounds without waxes. This effect becomes less significant for high CB content (greater than 33 phr), which can be seen by the developing of the respective curves in Figure 6. Therein, the volume fraction of CB is high compared to those of waxes so that the reinforcement clearly dominates the material’s behaviour.
The influence of pre-stretching on the volumetric behaviour is determined by exposing the specimen used in uniaxial tensile testing to hydrostatic pressure. The testing procedure is the same as in 3.1., whereas the specimens’ shape differs since they are cut out of plates which were exposed to uniaxial loading conditions to introduce the stress-softening effect. The results of this test series is shown in Table 2, the compounds with 33 phr CB are left out here. The influence of pre-stretching on the compression behaviour of a technical rubber compound (I to IV) is negligible, since the results lie within the standard deviation. On the other hand, the pre-stretching influences the compression behaviour of compounds without waxes which results in a decrease in bulk modulus of about 5 %. This may be due to the breakage of filler network and therefore a lower resistance against external loading.

Table 2. Resulting bulk moduli with and without pre-stretching.

| compound | bulk modulus [GPa] |
|----------|-------------------|
|          | without pre-stretching | with pre-stretching |
| I        | 2.68              | 2.65               |
| II       | 2.50              | -                  |
| III      | 2.30              | 2.28               |
| IV       | 2.17              | 2.17               |
| V        | 2.79              | 2.69               |
| VI       | 2.58              | -                  |
| VII      | 2.42              | 2.23               |
| VIII     | 2.26              | 2.13               |

3.3. Comparison of shear modulus and bulk modulus

The results obtained for hydrostatic compression tests as well as shear tests enable a determination of the ratio of the respective material parameters $K$ and $\mu$, which is crucial for the result quality of FE simulations (6). Since the bulk modulus affects these results significantly for pressure values greater than 10 bar, the linear approximation of $K$ is evaluated and compared to $\mu$. The initial shear modulus as well as the bulk modulus is obtained for each of the eight NR compounds. In Figure 7 the resulting $K/\mu$ is depicted for technical NR compounds (I to IV) with decreasing content of carbon black. The commonly made assumption of a bulk modulus being orders of magnitude higher than the shear respective modulus is confirmed, even though the ratio decreases with increasing content of CB. The higher the content of CB and therefore the reinforcement the more important becomes $K$ in relation to $\mu$, the ratio reduces to approximately two thirds compared to the NR without any CB. The shear stiffness increase under mechanical loading due to higher reinforcing filler content exceeds the increase in bulk stiffness. The assumption of a constant ratio of $K$ and $\mu$ independent of the filler content may lead to a significant deviation in FE results and therefore influences the accordance of simulation and test results [6]. This instance and therefore the not constant ratio emphasize the importance of a determination of all material parameters including the bulk modulus to achieve a satisfactory FE result quality, especially for confined rubber components.
4. Conclusion

The results presented show the influence of fillers in NR, carbon black and waxes like ageing inhibition or plasticisers, on the hydrostatic compression behaviour. Therefore, NR compounds with four different carbon black contents each with and without waxes are tested. All of the tested compounds possess the same characteristic dependence of hydrostatic pressure on volume reduction. For low volume strain a curvature results from free volume holes, which show lower resistance against compression compared to the bulk material and are therefore compressed primarily, ending in a linear curve progression at higher volume strain or pressure values greater than 10 bar, respectively. A reinforcement as known from mechanical testing is found for hydrostatic compression as well. Due to a higher bulk modulus of CB compared to NR and a decreasing number of free volume holes in compounds with higher CB content the bulk stiffness and therewith its modulus increases. The effects on shear stiffness proved more significantly compared to bulk stiffness. The stress-softening for NR compounds under uniaxial loading as well as its influence on the hydrostatic compression behaviour is determined. It is pointed out, that there is no relation between pre-stretching and subsequent compression detected for technical NR compounds. Furthermore, a comparison of the development of shear and bulk modulus related to the content of CB is drawn. The influence of the volumetric part in material modelling becomes more important with an increasing CB content. Carbon black enhances the shear stiffness significantly compared to bulk stiffness.

To confirm that free volume holes cause the obtained behaviour under hydrostatic pressure, swelling experiments are to be carried out. Therewith, the free volume of a specimen and the influence of fillers on it can be determined. Furthermore, positron annihilation lifetime spectroscopy (PALS) proved to be an adequate tool for a more precise identification of the number and size of free volume holes and is to be conducted. A comparison of these tests and the here presented results will enable a more precise understanding and determination of the occurring effects in NR.

References

[1] Mooney M 1940 *A Theory of Large Elastic Deformation* Journal of Applied Physics 11 p 11
[2] Ogden R W 1972 *Large Deformation Isotropic Elasticity - on the Correlation of Theory and Experiment for Incompressible Rubberlike Solids.* Royal Society of Applied Mathematics and Physics vol 326
[3] Kilian H G 1981 *Energy-Balance in Networks Simply Elongated at Constant Temperature* Colloid and Polymer Science 259 pp 1084-1091
[4] Heinrich G, and Kaliske M 1997 *Theoretical and Numerical Formulation of a Molecular Based Constitutive Tube-Model of Rubber Elasticity* Computational and Theoretical Polymer Science 7 pp 227-241

[5] Ogden R W 1984, *Non-Linear Elastic Deformations* (Chichester, Ellis Harwood Ltd.)

[6] Zimmermann J, and Stommel M 2012 *The Mechanical Behaviour of Rubber under Hydrostatic Compression and the Effect on the Results of Finite Element Analyses* Archive of Applied Mechanics 83 pp 293-302

[7] Hartmann S, and Neff P 2003 *Polyconvexity of Generalized Polynomial-Type Hyperelastic Strain Energy Functions for near-Incompressibility* International Journal of Solids and Structures 40 pp 2767-2791

[8] Mullins L 1947 *Effect of Stretching on the Properties of Rubber* Journal of Rubber Research 16

[9] Mullins L, and Tobin N R 1965 *Stress Softening in Rubber Vulcanizates. Part I. Use of a Strain Amplification Factor to Describe the Elastic Behavior of Filler-Reinforced Vulcanized Rubber* Journal of Applied Polymer Science 9 pp 2993-3009

[10] Harwood J A C, Mullins L, and Payne A R 1965 *Stress Softening in Natural Rubber Vulcanizates. Part II. Stress Softening Effects in Pure Gum and Filler Loaded Rubbers* Journal of Applied Polymer Science 9 pp 3011-3021

[11] Harwood J A C, and Payne A R 1966 *Stress Softening in Natural Rubber Vulcanizates. Part III. Carbon Black-Filled Vulcanizates* Journal of Applied Polymer Science 10 pp 315-324

[12] Harwood J A C, and Payne A R 1966 *Stress Softening in Natural Rubber Vulcanizates. Part IV. Unfilled Vulcanizates* Journal of Applied Polymer Science 10 pp 1203-1211

[13] Harwood J A C, and Payne A R 1967 *Stress Softening in Natural Rubber Vulcanizates. Part V. The Anomalous Tensile Behavior of Natural Rubber* Journal of Applied Polymer Science 11 pp 1825-1834

[14] Kahraman H, Weinhold G W, Haberstroh E, and Itskov M 2010 *Anisotroper Mullins-Effekt bei rüßgefüllten Elastomeren* KfK 3 pp 64-69

[15] Wood L A, and Martin G M 1964 *Compressibility of Natural Rubber at Pressures Below 500kg/Cm2* Journal of Research of the National Bureau of Standards Section a-Physics and Chemistry A 68 p 259

[16] Jobando V O, and Quarles C A 2007 *Effect of Cross-Linking on the Free Volume Properties of Natural Rubber* Physica Status Solidi C - Current Topics in Solid State Physics vol 4 Physica Status Solidi C-Current Topics in Solid State Physics 10 (A. P. Knights, P. Mascher and P. J. Simpson) pp 3759-3762