The influence of liquid rubber on selected properties of rubber compound and its vulcanizates

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Abstract. The aim of the work was to determine the influence of liquid rubber on selected properties of rubber compound and its vulcanizates. Due to the liquid form of this rubber, it is not possible to completely replace the conventional solid rubber used in the mixture because of problems in further processing. In four experimental tests, we used different amounts of liquid rubber in the recipe together with butadiene-styrene rubber and the compounds we mixed according to the general conditions. We studied the curing characteristics of prepared mixture and we measured the physical and mechanical properties of study vulcanizates and summarized the individual measured values for each parameter and suggested the greatest importance of the recipe for rubber practice.

1. Introduction

Nowadays, great focus is placed on the preparation of rubber compounds used in industry. The automotive industry is still setting the pace for several world economies and is subject to constant research and development progress [1]. Reducing rolling resistance or even greater emphasis on increasing the driving length of tires is now a common standard [2]. Therefore, introducing new technologies or the industrialization of new materials in the rubber compound segment is crucial. Their properties can be managed and adjusted by the change in raw materials or their exchange for new raw materials, which are characterized by special properties, such as, e.g., increasing the adhesion to metal parts or improving the dispersion of the filler, as the demand for high-fill silica compounds that meet the demand of the automotive industry, is dominant [3, 4]. The basic component of any rubber compound is always rubber. The choice of rubber depends on several factors. Depending on the requirements for the properties of the compound, natural or synthetic rubber, or a combination thereof, is used. Liquid rubber is still a revolution in the rubber industry [5]. The tread compound is in direct contact with the road and is exposed to sunlight, high wear and other negative effects, so it is necessary to use materials that slow down or improve the driving parameters of the tires. Such materials are antioxidants, antiozonants, organic and inorganic additives [6 – 8]. An important component is a filler. In the last stage of the rubber compounds preparation, a vulcanization system is an essential component. In this work, the aim will be to compare the properties of the rubber compound and its vulcanizates while changing the content of liquid rubber, which is still considered revolutionary new in the rubber industry [9 –10].
2. Experimental

2.1. Materials

The most important step is to choose a suitable recipe needed to prepare a suitable mixture (Table 1). The main component is a polymer, which always represents 100 phr. Other raw materials are converted to 100 phr of rubber using an equation. Butadiene styrene rubber from the synthetics was used. It is one of the most common rubbers in the rubber industry. It reduces tire wear and improves adhesion to the road [11]. In the mixture we choose, it is supplemented with liquid rubber in a certain ratio. It has less rolling resistance, fuel savings and shorter braking distances. Liquid rubber used in the rubber industry contains liquid isoprene rubber and liquid butadiene rubber. These highly viscous synthetic rubbers are based on isoprene, butadiene and styrene [12]. They are colorless, transparent and almost completely odorless, with a low content of volatile organic compounds. Liquid rubber types function as reactive plastificators but have a much higher molecular weight than conventional plastificators. It reduces the viscosity, which minimizes migration in the tire while improving the product’s shelf life [13]. The use of a liquid polymer during the rubber mixing phase significantly shortens the mixture’s preparation time while maintaining the rubber’s physical properties. The result is a product with lower processing costs. It has strong sticky and adhesive properties, increases processability and is characterized by a lower glass transition temperature. For the mixture to achieve the required properties and meet the required parameters of the rubber compound, it is necessary to use other raw materials. An important component is a filler. Since the filler content in the recipe is higher than the standard, we conclude that it is a highly filled silica mixture [14 – 15]. The vulcanization system is based on soluble sulfur and together with the vulcanization accelerators, an adequate vulcanization time is achieved. Without vulcanizing additives, the vulcanization process would not be possible and the tire would not be functional [16 – 17].

| Mixture component                        | Contents (phr) * |
|------------------------------------------|------------------|
| Rubber                                   | 100              |
| Fillers                                  | 0 – 200          |
| Plasticizer                              | 0 – 40           |
| Vulcanization activators and retarders   | 0 – 40           |
| Stabilizers – antioxidants, antiozonants, vosky | 0 – 9           |
| Vulcanizing system                       | 0.25 – 40        |
| Vulcanization accelerators               | 0.3 – 4          |
| Additives                                | 0 – 10           |

*(phr) parts per hundred of rubber

2.2. Mixing

By mixing on large-volume mixers, we can get a mixture with a volume of several hundred kilograms. We chose a smaller, low-volume Brabender mixer (Figure 2) for the test, which mixed for us only the necessary amount to test the samples [18].

![Figure 1. Brabender mixer](image-url)
For the preparation of the mixtures, three mixing steps were chosen. In particular, for better homogeneity of the mixture, incorporation of individual raw materials and reducing the degree of viscosity also brings better processing properties. This is the most energy-intensive but, in terms of production process efficiency, the best solution. In the first stage, most of the raw materials are added. Rubber, filler and chemicals were mixed. The mixing procedure was the same for all four tests. The mixing cycle lasted 443 seconds and the highest temperature reached was 148 °C. The main step of the first stage of mixing is silanization. The condition was to reach the silanization temperature and silanization time. The temperature is in the range of 140 – 160 °C. Its value affects some parameters, such as hardness or elasticity. We used the pressure of the log to reach such a high temperature. It was necessary to weigh the mixed mixture, measure the temperature with a thermostat and extrude on a twin-cylinder to achieve the desired shape and thickness. The mixture had to be allowed to rest for at least 4 hours before the next mixing step. The second stage of mixing is used only in some cases. Only the cooled base stage is added to the mixing device in this mixing stage without additional raw materials. The time required for mixing was much shorter than in the first stage – 153 seconds and the highest temperature reached was 115 °C. This step was mainly used to reduce the viscosity and improve the homogeneity of the mixture [19]. The third and final step is important in terms of adding a vulcanization system. In one step, vulcanizing additives were added, including a vulcanizing agent, in our case sulfur, and vulcanization accelerators. The maximum temperature reached during mixing was 97 °C. After the extrusion, it was important to check the homogeneity of the mixture, measure the resulting temperature, weigh the mixture, and adjust the mixture on a twin roll to the desired shape to take samples for testing [20].

2.3. Methods of testing of rubber blends and vulcanizates properties
Rheological and curing characteristics of prepared rubber blends were measured on the instrument MDR 160 (moving die rheometer) at the temperature of 160 °C for 60 min. MDR 160 is intended for measuring the rheological properties of vulcanizable elastomers during the process of their vulcanization. The vulcanization curve is the output of the measurement and it is possible to determine the behavior of the material during processing and vulcanization. We determined t10 (beginning of vulcanization), which the time is to reach a 10 % increase from the minimum torque (ML), and t90 (optimal vulcanization time) - which is the time to reach a 90% increase from the ML. The choose properties of vulcanizates (elongation at break, hardness, density, modul, stiffness and rebound resilience) were determined according to standards.

3. Results and discussion
Due to the processability and complexity of the mixture properties, the conformity of all properties according to the customer’s definition must be ensured. By changing one parameter, we almost always influence other parameters, which greatly influence the resulting tire properties. We can influence the properties of the mixture by the process of preparing the mixture or by modifying the recipe. Four mixtures were prepared – RF1 (standard), LR2, LR3 and LR4. Different amounts of liquid rubber were used in the prepared rubber blends. The amount of liquid rubber was reduced with each dose until completely eliminated from the recipe in the last batch tested (Table 2).

| Samples | RF1 | LR2 | LR3 | LR4 |
|---------|-----|-----|-----|-----|
| Added liquid rubber [phr] | 13.3 | 8.9 | 4.5 | 0 |
| Added liquid rubber [%] | 100 | 67 | 34 | 0 |

3.1. The properties of rubber blends
From the results of vulcanization characteristics (Figure 2, Table 3), we conclude that the value of the beginning of vulcanization t10 increased until LR3.
In LR4, where the test material (liquid rubber) was completely excluded from the formulation, the $t_{10}$ value decreased and reached the lowest value. In LR3 with the highest value $t_{10}$, better processing of the mixture for extrusion is expected. The vulcanization characteristic of $t_{90}$, also called the vulcanization optimum, has the same trend as the value of $t_{10}$. The lowest value of $t_{90}$ was measured in LR4, where an increase in the efficiency of the vulcanization production process can be expected. The results are shown in Table 3.

### Table 3. Values of MDR 160

| Samples | Rf1 | LR2 | LR3 | LR4 |
|---------|-----|-----|-----|-----|
| $t_{10}$ (min) | 3.32 | 3.50 | 3.50 | 3.25 |
| $t_{90}$ (min) | 7.79 | 8.06 | 8.34 | 7.42 |

### 3.2. The properties of vulcanizates

The sample Rf1, used as the standard, achieved the lowest hardness compared to other samples. The hardness graph (Figure 3) indicates that the liquid polymer also has the function of a plasticizer in the mixture since the hardness of the mixture increased by eliminating the amount of liquid polymer. Further samples, therefore, achieved a higher hardness compared to Rf1.

We assume that increasing values of compound hardness could improve the driving characteristics and service life of the tire. However, with increasing hardness, we increase the mixture’s viscosity while causing worse processing properties and increasing hardness decreases the value of the rebound. The
lowest value is 62.25 Shore A, which is still sufficient hardness for the rubber compound and no visibly negative driving properties are expected. The batching of liquid rubber fundamentally affects the properties of rubber compounds. Values of hardness are given in Table 4.

### Table 4. The hardness of vulcanizates Rf1, LR2, LR3 and LR4

| Samples | Rf1 | LR2 | LR3 | LR4 |
|---------|-----|-----|-----|-----|
| Hardness (Shore A) | 62.25 | 66.70 | 68.00 | 69.10 |

The table 5 shows the measured values of the rebound resilience, stated in %. On the graph (Figure 4), we can see the tendency of a gradual decrease of the value of the rebound resilience in direct proportion to the gradual elimination of the material tested by us. From the values, we can conclude that the highest value was reached by Rf1, representing the highest ratio of liquid rubber in the recipe, by almost 2 % compared to LR4, from which the liquid rubber was completely eliminated.

![Figure 4. Rebound resilience of vulcanizates Rf1, LR2, LR3 and LR4](image)

Therefore, we can estimate the large effect of liquid rubber on the given tested parameter of the mixture. The value of the rebound resilience indicates the influence on the tire’s rolling resistance to the road, which affects the energy values of the tire. The higher the value of the rebound resilience, the lower the rolling resistance and thus the lower consumption.

### Table 5. Rebound resilience of vulcanizates Rf1, LR2, LR3 and LR4

| Samples | Rf1 | LR2 | LR3 | LR4 |
|---------|-----|-----|-----|-----|
| Rebound resilience [%] | 18.86 | 18.01 | 17.47 | 17.06 |

The stiffness of studied vulcanizates is one of the parameters that are part of the tensile test. The lowest value of 13.24 MPa is represented by Rf1. As the amount of liquid polymer decreases, we observe an increasing stiffness trend after LR3, as seen in the graph (Figure 5).
Figure 5. Stiffness of vulcanizates Rf1, LR2, LR3 and LR4

A slight decrease occurred in the last sample, where no test material was present in the mixture. Values of stiffness are given in Table 6.

Table 6. Stiffness of vulcanizates Rf1, LR2, LR3 and LR4

| Samples | Rf1  | LR2  | LR3  | LR4  |
|---------|------|------|------|------|
| Stiffness [Mpa] | 13.24 | 15.10 | 16.43 | 15.20 |

Another parameter evaluated from the tensile test is elongation at break. The values measured for the four samples from each mixture represent different values. As with stiffness, the trend changed in direct proportion to the change in liquid rubber batching. While in the first Rf1, the value was 385.01%, in the other two samples, significantly higher values were measured (Figure 6).

Figure 6. Elongation at break for studied vulcanizates

The decrease occurred during the last LR4, where there was no liquid rubber in the recipe. We measured the lowest value of elongation at break without this material, which confirmed the deteriorated homogeneity of LR4. Based on stiffness and elongation at break values, we conclude that LR4 was the toughest material, which is confirmed by the viscosity results. Values at elongation at break are given in Table 7.

Table 7. Elongation at break of vulcanizates Rf1, LR2, LR3 and LR4

| Samples | Rf1  | LR2  | LR3  | LR4  |
|---------|------|------|------|------|
| Elongation at break [%] | 385.01 | 431.99 | 436.63 | 376.08 |
We monitored the values of modulus: M100 (100%), M200 (200%), M300 (300%), selected during our measurement (Table 8). In the case of tread compounds, M300 is most often evaluated, representing an elongation of the test sample by 300 % (Figure 7).

![Figure 7. M300 of studied vulcanizes](image)

Table 8. Modulus of vulcanizates

| Samples   | Rf1 | LR2 | LR3 | LR4 |
|-----------|-----|-----|-----|-----|
| Modul 100 [Mpa] | 2.32 | 2.4 | 2.64 | 2.83 |
| Modul 200 [Mpa] | 5.58 | 5.72 | 6.34 | 7.02 |
| Modul 300 [Mpa] | 9.62 | 10.54 | 11.54 | 12.84 |

The measured density values of studied vulcanizates, which are graphically represented on figure 8, show an increasing trend. While Rf1 with 100 % addition of liquid rubber in the recipe represented the lowest measured density of 1.238 g/cm3, the highest values were obtained in LR4.

![Figure 8. Density of vulcanizates](image)
The reduction of liquid rubber in the recipe, in our case also the plasticizer, increased the toughness of the mixture. The results of density of vulcanizates are given in Table 9.

| Samples | Rf1   | LR2   | LR3   | LR4   |
|---------|-------|-------|-------|-------|
| Density [g/cm³] | 1.238 | 1.244 | 1.248 | 1.252 |

4. Conclusion
This work dealt with the influence of liquid rubber on selected properties of rubber blend and its vulcanizates. Four samples with different amounts of liquid rubber were prepared. The samples were marked Rf1 to LR4, from the largest amount of liquid rubber in the recipe to the complete reduction of this material. We evaluated the expected effect of liquid rubber in the rubber compound as well as the effect on the resulting properties of the tire. Rf1, which contained the largest amount of liquid rubber, achieved the lowest measured hardness due to the addition of liquid material. The rebound resilience was the highest value in Rf1, which affects the consumption. This recipe has the best processing properties due to its lower viscosity. In LR4, which did not contain liquid rubber, the highest hardness values were measured, thus improving the driving characteristics. However, other parameters showed worsened values. The non-dosing of the liquid material, which also served as a plasticizer in the mixture, impaired the rebound resilience, thus increasing the tire’s rolling resistance. The less favorable results were also measured at density, where higher stiffness of the mixture can cause deteriorated processing properties. Increasing the amount of liquid rubber favorably affected the rebound resilience. The addition of liquid rubber reduced the hardness, but the values were not significantly low. Therefore we cannot state deteriorating driving characteristics. Liquid rubber did not have a significant effect on the vulcanization characteristics. Due to the liquid form of this rubber, it is not possible to completely replace the conventional solid rubber used in the mixture because of problems in further processing. From the above results of testing individual parameters, we can conclude better final properties of the tire using a mixture containing liquid rubber.

5. References
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