The effect of various alternative filler granularity on the properties of elastomeric vulcanizate

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Abstract. This work deals with the influence of different alternative filler granularities or fractions (size) on properties of real elastomeric blend. Alternatively, the filler was subjected to a sieve analysis to obtain individual fractions of filler as well as to determine the ratio of individual fractions in a determined amount of alternative filler. The main objective was to evaluate the effect of the granularities on the basic properties of the elastomeric blend. Prepared elastomeric blends were studied in terms of their properties and vulcanization characteristics. The resulting vulcanizates were tested from the aspect of hardness and rebound resilience. In the case of commercially available fillers (e.g. carbon black), the granularity is a significant parameter affecting the properties of the elastomeric blends. From the results of tests for the prepared materials, it is possible to determine the most suitable granularity of the alternative filler for the preparation of elastomeric materials. In relation to given suitable granularity, the application of the basic alternative filler is not suitable to achieve better quality parameters. The results show a significant granularity effect of the alternative filler on the properties (hardness, rebound resilience, rheological, vulcanization characteristics) of the elastomeric vulcanizate.

1. Introduction
Elastomeric blends have undergone a major development over the past decades in relation to the development of blends for special applications as well as the new trend of blends for green tires. In the most cases of elastomeric blends, the filling (with filler) of the blends plays a major role. The filler often improves the processability of the blend and modifies the resulting properties of the elastomeric vulcanizate (hardness, mechanical properties, rolling resistance, etc.), while the economic aspect (reducing the cost) has to be also taken into account during processing. Fillers are commonly added into the polymer to create new functional properties which are not typical for the polymer matrix. The incorporation of the filler into the elastomeric matrix and its effect on the elastomeric blend or on the elastomeric vulcanizate depends on several factors, such as: type of filler, particle size, surface area, particle shape and fill factor of the elastomeric blend. From the industrial processing aspect, the effect of the most commonly used filler – carbon black on the vulcanizate properties represent the most explored and reviewed research area. The carbon black proportionally increases the properties of the vulcanizate with a decreasing particle size. Enhancing effect magnitude also increases with higher carbon black content. For some alternative filler that have been used for the last decades, the particle size effect has not been examined to the required depth.

Since some by-product or waste from different industries (not only from rubber industry) can be used as alternative fillers, the particle size or its granularity play important role and the influence of
these two mentioned factors is reflected in the properties of the resulting vulcanizate or product. This work deals with the particle size of the alternative filler and alternative filler granularities from the aspect of the influence on the properties of the vulcanizate.

2. Materials and methods

2.1. Sieve analysis of alternative filler

Sieve analysis is a method of determining the particle distribution, usually expressed as a percentage of the mass of particles left on each of a series of sieves with decreasing mesh size. The analysis was performed with Sieve Shaker AS 200 control, using sieves with a mesh size of 40, 32, 25 μm. Fractions with size >40 μm and <25 and fractions in interval of 40–32 μm and 32–25 μm were obtained by sieve analysis [1]. To determine the fraction (content of individual fractions) in the alternative filler, 100 grams of the alternative filler was predetermined as the reference weight (reference sample). The selection of the reference sample is very important because if the required weight of selected sample is exceeded, there will not be the needed contact of particles with the sieve. The investigation confirmed that, the excess of reference sample weight increases analysis error [2]. Alternative filler was subjected only to fine crushing before sieve analysis to disrupt clusters. The special attention was paid to fact that crushing is not allowed to be the affecting factor of the result from the sieve analysis.

2.2. Preparation of rubber blends with content of alternative filler

For this work, the series of elastomeric blends were prepared according to the prescription in table 1. In all prepared blends, the content of the alternative filler was the same to ensure the possibility of mutual comparison. The difference of individual blends was based on the different particle size of the alternative filler that was used for preparation of the given elastomeric blend. Plastograph Bradender laboratory mixer was used to prepare elastomeric blends. The blends were prepared in two steps at 90 °C. The alternative filler was added to the matrix together with commonly used filler – carbon black. The mixing time for the fillers was determined for 180 s to ensure sufficient incorporation of fillers in the matrix [3]. In order to increase the homogeneity of the blends after each mixing step, an additional homogenization was carried out by a laboratory twin roller for each blend. After the second mixing step, the blend was left at room temperature for 24 hours [4]. The prepared blends were designated according to the alternative filler fraction that was used for preparation of the blend.

| Ingredients                  | Quantity of ingredients (phr) |
|------------------------------|-------------------------------|
| SMR 10                       | 100.00                        |
| Carbon black (N339)          | 30.00                         |
| Alternative filler (ENERGO)  | 47.32                         |
| Zinc oxide                   | 5.00                          |
| Stearic acid                 | 2.00                          |
| Sulphur (oiled)              | 2.50                          |
| Accelerator (TBBS)           | 1.50                          |

2.3. Rheological and vulcanization characteristics

Vulcanization characteristics, as a function of time and temperature, describe chemical processes. In the case of elastomeric blends, the given vulcanization process includes the crosslinking process and its course up to the maximum crosslinking effect as well as the reactions after the crosslinking process (e.g. reverse, plateau, marching module).

Based on the reason for the possible industrial application of the prepared elastomeric blends, with an emphasis on economic and time aspects, a vulcanization temperature of 160 °C was chosen. Determination of rheological and vulcanization characteristics was performed with the help of the
Rubber Process Analyzer RPA 2000 in specialized laboratories at the Faculty of Industrial Technologies in Púchov. Rheology involves the study of deformation and mass flow. The aim is to establish relationships between stress and deformation of materials, where neither Newton's Law nor Hooke's Law is enough to explain their mechanical behaviour [5, 6]. The selected and monitored characteristics include: optimum cure time ($t_{C90}$), scorch time ($t_{S02}$), minimum torque ($M_L$), maximum torque ($M_H$).

2.4. Determination of hardness ShA
The hardness of the vulcanizates containing the alternative filler was determined using a Shore A handheld hardness tester. Samples were measured according to ASTM [7].

2.5. Determination of rebound resilience
The determination of the rebound resilience was carried out by impacting the pendulum on the surface of the elastomeric vulcanizate sample and by calculating the relative kinetic energy ($R$) which was needed to reach the height designated as $h_2$, while the initial or original height was designated as $h_1$ [8]:

$$R = \frac{h_2}{h_1}$$

The energy supplied to the impactor in the form of mechanical vibration caused by the impact should not be attributed to the energy losses in the sample. Determination of rebound resilience of the prepared vulcanizates was performed by the Polymertest apparatus with a digital indicator of rebound resilience (%).

3. Results and discussion
In results and discussion, there are summarized the results of sieve analysis, rheological and vulcanization characteristics, hardness values and rebound resilience values. For better orientation and comparison of the results, the measured values of individual properties were processed graphically.

3.1. Sieve analysis
The percentage content of the individual fractions from the reference sample of the alternative filler as a result of the sieve analysis is shown in table 2. From the results, it can be concluded that the largest fraction (>40 μm) of alternative filler forms the highest percentage, namely 60.88 %, compared with reference sample. It is interesting fact that the smallest fraction of the alternative filler (<25 μm) does not form the smallest percentage in comparison with the reference sample. The sieve analysis results can be easily changed by adding an alternative filler if the crushing process is prior to the sieving process. The proportion of the fractions, their amount in the reference sample as well as the necessity of including the crushing process for the alternative filler processing will depend on the influence of the individual fractions on the desired properties of the elastomeric blend and the vulcanizate.

| Fractions (size) | Weight of fraction (g) | Percentual content (%) |
|------------------|------------------------|------------------------|
| >40 μm           | 60.88                  | 60.88                  |
| 40–32 μm         | 17.28                  | 17.28                  |
| 32–25 μm         | 8.25                   | 8.25                   |
| <25 μm           | 10.36                  | 10.36                  |

3.2. Rheological and vulcanization characteristics
The measured values of rheological and vulcanization characteristics are recorded in table 3, and for better clarity, they are processed graphically in figure 1 and figure 2. The each one fraction of the alternative filler, used for preparation of elastomeric blends, will serve as a criterion for comparing the individual elastomeric blends, including the reference sample. The first characteristic is represented by
the study of minimum torque – measure of the stiffness of the unvulcanized tested sample taken at the lowest point of the curve [9].

Table 3. Results of rheological and vulcanisation characteristic.

| Filler fraction | Blend name | Minimum torque | Maximum torque | Scorch time | Optimal cure time |
|-----------------|------------|----------------|----------------|-------------|------------------|
|                 |            | $M_l$ (dNm)    | $M_h$ (dNm)    | $t_{s02}$ (min) | $t_{c90}$ (min) |
| >40 μm          | 1.48       | 17.5           | 1.58           | 3.62        |
| 40–32 μm        | 1.81       | 17.84          | 2.05           | 3.76        |
| 32–25 μm        | 1.7        | 17.71          | 2.09           | 4.66        |
| <25 μm          | 1.72       | 17.13          | 2.27           | 4.11        |

From measured values of minimum torque, it is possible to see the effect of the size of the alternative filler. As the particle size of the alternative filler decreases, the minimum torque value increased, compared to the torque value of the elastomeric blend with the largest fraction (size) of the alternative filler. Since the minimum torque indicates the stiffness of the mixture, it can be seen that a smaller fraction of the alternative filler led to the increase of the stiffness of the blend at the beginning of the vulcanization process. The greatest value of the minimum torque was achieved for a mixture with a filler particle size of 40–32 μm. Moreover, the blends containing fillers with a particle size of 32–25 μm and <25 μm achieved similar results in relation to the minimum torque. The maximum torque results show a similar course to the minimum torque. Maximum (plateau, or highest) torque – measure the stiffness or shear modulus of the fully vulcanized tested sample at the vulcanization temperature [9]. The highest measured maximum torque was achieved for a blend of 40–32 μm. By reducing the particle size of the alternative filler, the particle distribution per unit weight increases. A larger number of particles may cause a reduction in the mobility of the rubber chains in the matrix, resulting in an increase in stiffness [10]. The values of the maximum torque are not increased proportionally with the fraction decreasing of the alternative filler – in addition, it is possible to see some stabilization after initial increase of the values for blends of 32–25 μm, <25 μm, excluding the blend with 40–32 μm fraction where the value increase without any stabilisation was observed.

Figure 1. Measured values of maximal and minimal torque.

3.3. Curing characteristics include Scorch time ($t_{s02}$) and Optimal cure time ($t_{c90}$)

Scorch time ($t_{s02}$) – time of rise by two torque units above the minimum and it represents scorch safety time. By using the rise by two units instead of by one ($t_{s1}$ scorch time), it is possible to achieve a more accurate indicator of true scorch time. However, the true scorch time is a little more delayed in time, compared with $t_{s1}$ scorch time [11].
Optimal cure time \( (t_{90}) \) – this is the sufficient cure time for the compound to reach 90% of the required cure. This is another characteristic for evaluation cure rate. Some compounds can have similar scorch safety time but significantly different optimal cure time [11].

From the graphical representation of the measured values (figure 2), it can be seen that the scorch time value for the blends increased with decreasing fraction (size) of the alternative filler used for preparation of the blend. The increase in the scorch time value can be perceived from two points of view: industrial (the longer scorch time ensures perfect filling of the mould even for shape-complicated articles) and economical (the time required for the production of the product increases and thus increases the costs of production). In relation to the economical point of view, in the industrial application of the blend with the specified filler fraction, it is still possible to modify the vulcanization system and thereby reduce the scorch time values of the blend as well as the economic costs but with an impact on the properties of the resulting vulcanizate (e.g. hardness). The optimal cure time is also one of the characteristics affected by the size of the alternative filler. The graphical representation of the results in figure 2 reflects that the value of the optimum vulcanization time increased with decreasing the fraction (size) of the alternative filler. It can be seen again that the values of the optimum cure time were stabilized for blends of 32–25 μm, <25 μm. However, in order to confirm the correctness and reliability of the values for optimal vulcanisation, it would be necessary to split the last and thus the smallest fraction of the filler into several fractions. Since the alternative filler comprises SO₄, which joints to the vulcanization process, it is important to point out that decreasing filler fraction leads to higher number of SO₄ groups which are able to be present at the vulcanization process. Increasing the availability of SO₄ during the vulcanization process means the formation of more cross-links and thus there is extending of the optimum cure time. Measured hardness values can also be used to verify the effect of particle size (fraction) on resulting properties of blend and vulcanizate, where the hardness value increases with decreasing the particle size, indicating a greater number of cross-links (it is similar to hardening of the blend by vulcanization system) [12].

![Figure 2. Scorch time and optimal curing time values.](image)

3.4. Hardness measuring results

The measured hardness values of the prepared blends with different fractions of the alternative filler are recorded in Table 4 and graphically processed in figure 3 to give a better overview of the effect of the individual alternative filler fractions on the hardness value of the prepared vulcanizates. From the graphic processing, we can see an increasing trend of hardness values of prepared vulcanizates. At the same time, the increasing trend is supported by the confirmation that alternative fillers are involved in the vulcanization process. The particle size of the filler also affects the hardness value of the
vulcanizates. Since the particles are smaller and their number per unit of weight is higher, it is possible to ensure a more even distribution of the particles in the blend (better dispersion) [13].

| Filler fraction / Blend name | Hardness (ShA) |
|-----------------------------|---------------|
| >40 μm                      | 61.06 ± 0.27  |
| 40–32 μm                    | 62.4 ± 0.29   |
| 32–25 μm                    | 62.8 ± 0.31   |
| <25 μm                      | 63 ± 0.31     |

Figure 3. Measured values of hardness (ShA)

3.5. Rebound resilience results

The rebound resilience value of the elastomeric blends decreases with increasing the filler content in blend and it causes an increase of the blend hardness and a loss of elasticity. If different fractions of the alternative filler are always added in the same volume to the blend, it can be seen that the rebound resilience value increases (only with the exception of blend with particle size of 25>μm) [14]. Increasing the rebound resilience values demonstrates that the alternative filler and its individual fractions are not only mechanically mixed into the polymer matrix, but it can be assumed that the given fractions play the significant role for crosslinking with the polymeric matrix. Based on the mentioned fact, the alternative filler broke the rule that the rebound resilience value commonly decreases with increasing hardness.

| Filler fraction / Blend name | Rebound resilience (%) |
|-----------------------------|------------------------|
| >40 μm                      | 59.04 ± 0.51           |
| 40–32 μm                    | 59.25 ± 0.16           |
| 32–25 μm                    | 59.43 ± 0.43           |
| <25 μm                      | 58.92 ± 0.16           |
4. Conclusion
The given introduced paper was based on investigation of the alternative filler with the predetermined fractions (particle sizes) and its effect on the characteristics for prepared elastomeric blends and vulcanizates, including the mutual comparison of the given blends with the different alternative filler fractions (particle sizes). Based on the investigation, it can be concluded that there was the effect of the fraction (particle size) on the selected properties of the prepared elastomeric blends and vulcanizates. The mentioned effect of the fraction (particle size) was investigated from the aspect of rheological and vulcanization characteristics as well as hardness and rebound resilience. The sieve analysis was used for determination of the individual fractions in the reference sample. The values of rheological and vulcanization characteristics were being increased with the decreasing of the alternative filler fraction (particle size). In relation to the investigation of the alternative filler, the increase of the values resulting from the decreasing of the fraction (particle size) could be also seen in the values of the hardness and rebound resilience referring to the prepared vulcanizates.

Using the graph in figure 5, it is possible to select the most suitable blend for the industrial application, including the selection of the required properties. Moreover, it is also possible to see the overall trend of individual properties in dependence on the used alternative filler fraction (particle size).
5. References

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