

## 필러재료의 변화에 따른 NR-SBR 타입 엘라스토머 기반 고무재료의 기계적물성

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## Effect of Changing of Filling Materials in NR-SBR Type Elastomer Based Rubber Materials on Mechanical Properties

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**Abstract:** The effects of different filling materials and stabilizers in polymer based materials that are used as shoe soles in the shoemaking industry on the mechanical properties (strength, failure, tensile, tearing, bending etc.) of the final products have been examined in this study. Natural rubber (NR RSS3) and styrene-butadiene rubber (SBR 1502) were used as the main matrix material. New compounds were formed by replacing the fillings in the general compound of the existing factory (SiO<sub>2</sub>, CaCO<sub>3</sub>) with 40% (1200 g) blast furnace flue dust, rice husk, reclaimed rubber (recycled) and wood ash. Comparison of the new compounds with the existing compounds revealed a decrease in hardness, density, dimension stability, bending, tearing, % elongation and failure strength and an increase in wearing.

**Keywords:** NR-SBR, rubbers, mechanical properties, fillings, elastomer.

### Introduction

Natural and artificial rubbers are widely used in various industries, particularly in shoe sole making, due to their superior properties. Various organic or inorganic materials are used as filling materials to give rubber based polymeric materials desired properties. The aim of this study is to use unused materials as filling materials and protect our environment from waste (non-recyclable) materials. The benefits of these filling materials are low cost and easy availability. We studied the effects of filling materials on mechanical properties in elastomer based materials.

Natural rubber (NR) is an interesting material with commercial success due to its excellent physical properties (i.e., high mechanical strength, low heat build up, excellent exibility, and resistance to impact and tear), but also to the fact that NR is a renewable resource. However, NR has also some draw-

backs as, for instance, low ame resistance, sensitivity to chemicals and solvents (ozone and weathering), mainly due to its unsaturated hydrocarbon chain structure and its non-polar character, which cause limitation in variety of applications.<sup>1</sup> A review of the literature have shown that various materials such as mica powder, wollastonit, glass sphere, glass fiber, nano-clay, calcium carbonate, talc, carbon black are used as filling materials.<sup>2,3</sup> High cost of filling materials has led the people to seek cheaper filling materials. As for as the know ledge of authors there is no study on the use of wood ash and blast furnace flue dust as filling materials in the literature. Beside, there is a limited body of research on rice husk and reclaimed rubber.<sup>4,5</sup>

PP/EPDM/White rice husk reduced product deformation in rubber. Furthermore, they reported that it enhanced material viscosity and melting viscosity and that smooth surfaces were obtained in a 4% filling composite.<sup>6</sup> Superior rheological and dynamic mechanical properties can be obtained by the use of composites in which grinded waste rubber (reclaimed rubber) is replaced with certain ratios of carbon black.<sup>7</sup> Bending capa-

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bility, failure strength and hardness should be enhanced while material cost should be reduced to achieve the desired properties in the use of filling materials in elastomers.<sup>8</sup>

Effects of wood flour on rheological, mechanical and wearing effects in NR compounds, compared the values with those obtained with carbon black. The researchers used 15-30% wood flour as filling material in NR. They reported that materials with a grain size of 250-300  $\mu\text{m}$  did not deteriorate wearing properties; they increased failure strength and that wood flour can be used as a semi-reinforcing filling material in NR composites.<sup>9</sup> Analyzed tensile, compressive and impact resistance values by adding 2-10% peanut husk powder (wood cellulose) into polyurethane material. The quantity of filling material increased, tensile strength increased as well. Filling material had a negative impact on impact resistance. As the quantity of filling material increased, a decrease was observed in impact resistance. 4% filling material gave the best result in compressive strength, while 8% filling material gave the worst result. In conclusion, the researchers reported that it can be used as a filling material in polyurethane.<sup>10</sup> Material type, type of filling material and grain size were important parameters on mechanical properties.<sup>11</sup> Reinforced NR/SBR rubber with nanoclay filling and analyzed the effects on mechanical and thermal properties. The researchers observed that as %weight ratio of nanoclay increased, hardness increased as well, however, cold tearing strength decreased.<sup>12</sup>

In a study on rheological behavior of mineral fillings in shoe sole materials, Jolene *et al.*, used 10% mica powder or 10% glass sphere instead of calcium carbonate ( $\text{CaCO}_3$ ) in SBS block copolymer and studied the changes in mechanical properties of the material. They reported that glass sphere yielded the best result (5.8 MPa);  $\text{CaCO}_3$  filled composite gave the value of 5.49 MPa and mica powder filled mixture gave the value of 5.41 MPa. In elongation at break tests, glass sphere filled composite gave the value of 630, calcium carbonate filled composition gave the value of 685; mica powder filled mixture gave the value of 650. As for the hardness values of the obtained SBS copolymer composites, they reported that all three materials were identified as 62 Shore A; wearing ratios of glass sphere, filled materials,  $\text{CaCO}_3$  filled materials and mica powder filled composites were found to be 273, 307 and 378  $\text{mm}^3$ , respectively. Tearing strength values of glass sphere,  $\text{CaCO}_3$  and mica powder filled composites were found to be 25, 23, and 24 N/m respectively.<sup>13</sup>

Studied NR/SBR composite ratios and the effect of  $t$  transition temperature of silica dioxide ( $\text{SiO}_2$ ) materials on these

composites. The highest  $t$  transition temperature was determined in alloys which contained equal amounts of NR/SBR rubbers. They observed that  $t$  transition temperature increases as %weight ratio of  $\text{SiO}_2$  increases.<sup>14</sup> Used modified phosphate instead of carbon black. They observed that mechanical properties improved and vulcanization times decreased.<sup>15</sup> Examined water intake property of nanoclay filling support to NR/SBR rubber structure and observed that increases in nanoclay weight amount decreased temporal water permeability properties of the rubber.<sup>16</sup>

Ge *et al.*, to improve the compatibility of bentonite with rubber matrix, organo-modified bentonite was synthesized with a silane coupling agent, [3-(2-aminoethylamino)propyl]trimethoxysilane (AEAPTMS) in the suspension of bentonite. Results showed that the concentration of hydrochloric acid and  $\text{H}_2\text{O}$  in the synthesis had significant influence on the modification of bentonite, which further contributed to the properties of the composites. Filled with 20 phr modified bentonite, the tensile strength and elongation at break of the rubber increased from 1.95 to 4.8 MPa and 300 to 500%, respectively.<sup>17</sup>

## Experimental

NR RSS3 and SBR 1502 were selected as rubber material. General (G) form of  $\text{SiO}_2$  and  $\text{CaCO}_3$  filling materials were replaced with new filling materials which are unrecyclable or cannot be used when recycled as they reduce the quality such as reclaimed rubber (GRR), blast furnace flue dust (GBFFD), wood ash (GWA) and rice husk (GRH). 40% (1200 g) new filling materials were added to the formula according to rubber amount. The formulae (compositions) are presented in Table 1.

**Filling Materials.** Granular materials in very small sizes that are added into rubber material in powder form are called filling materials. They are used to reinforce the rubber, improve its workability and to form cheap composites. Empirical studies used blast furnace flue dust, wood ash and rice husk as filling materials for the time. Reclaimed rubber (recycled) has been previously used as a filling material.

**Additives.** Materials that are added in small quantities to create bond formation in rubber, prevent hardening during furnacing or to enhance wearing property of unburnt paste. Additives include vulcanization materials (accelerators, activators, retarders), softeners (oils), process facilitators (hydrocarbons, fatty acids, synthetic resins, organic thio composites), ageing preventives and protectors (antiozonants, antioxidants), swell-

**Table 1. Composition of Rubber Compounds**

Filling materials	G	GWA	GRH	GRR	GBFFD
Natural rubber (NR RSS3)	1500	1500	1500	1500	1500
Styrene-butadiene rubber (SBR 1502)	1500	1500	1500	1500	1500
Calcium carbonate (CaCO <sub>3</sub> )	800	-	-	-	-
Silica dioxide (SiO <sub>2</sub> )	1000	-	-	-	-
Wood ash	-	1200	-	-	-
Rice husk	-	-	1200	-	-
Reclaimed rubber	-	-	-	1200	-
Blast furnace flue dust	-	-	-	-	1200
Poachers					
Zinc oxide	90	90	90	90	90
Sulfur	45	45	45	45	45
Stearic acid	45	45	45	45	45
Polyethylene Glycol (PEG 4000)	60	-	-	-	-
Accelerators					
Dibenzothiazole disulfide (DM)	30	30	30	30	30
<i>N</i> -Cyclohexyl-2-benzothiazole sulfenamide (CZ)	30	30	30	30	30
Diphenyl guanidine (DPG)	30	30	30	30	30

ing agents, dyes (pigments) odorants and special purpose substances.

In this study, 1% dibenzothiazole disulfide (DM), 1% *N*-cyclohexyl-2-benzothiazole sulfenamide (CZ), 1% diphenyl guanidine (DPG) was used as powder accelerator (accelerator); 3% sulfur and 3% zinc active were used as poachers and 1.5% stearic acid was used as process facilitator.

At preparation stage, external environmental conditions considered for all formulae; temperature was kept at 23±2 °C and relative humidity was kept at 50±5. NR/SBR rubbers were placed in banbury. Paste was prepared by adding filling materials, poachers and accelerators respectively at appropriate pressure and temperatures for the type of rubber product to produce a homogenous mixture.

In the next stage, after keeping the paste for 24 hrs, the paste was placed in vulcanization furnace molds (mold dimensions: 180×180×3 mm<sup>3</sup>) and furnaceed for 5 min under 160 bar pressure and 160 °C temperature. The products removed from the molds were kept for 24 hrs and then cut according to the standards of the tests.

Bending, density, hardness, wearing, dimension stability, % elongation, failure strength, tearing tests of test samples were performed in accordance with standards. Test results were compared to each other and with those of the original formulae.

## Results and Discussion

New compounds and the general compound were termed according to filling materials they contained as indicated in Table 2.

Results of the tests that were performed according to ISO 2781 density and EN 12772 dimension stability methods. Density should not exceed 1.5 g/cm<sup>3</sup> according to international standards (IS 5676). Although the density of the G compounds was 1.2 g/cm<sup>3</sup>, density values of new compounds varied between 1.19 and 1.02 g/cm<sup>3</sup>. These results are in a good agreement with that previously obtained study.<sup>18</sup> Due to the lower density of the used filling materials from SiO<sub>2</sub> and CaCO<sub>3</sub> it leads to decrease compounds densities. It was found that GRH had the lowest density and the density of GRR decreased by 15%. Density of GBFFD formulae decreased by

**Table 2. Abbreviations of Compounds**

<b>G</b>	General compounds
<b>GWA</b>	40% Wood ash
<b>GRR</b>	40% Reclaimed rubber
<b>GRH</b>	40% Rice husk
<b>GBFFD</b>	40% Blast furnace flue dust

1.18 g/cm<sup>3</sup>-1.6%. Even the density of GWA formulae which had the highest density, decreased by 1.19 g/cm<sup>3</sup>- 0.83%. Dimension stability test which was performed in accordance with EN 12770 standard norm revealed that size change was 0.94 mm<sup>3</sup> in G; however, it was between 1.33 and 0.27 mm<sup>3</sup> in G. It was observed that GRH had the best dimension stability, while GWA had the worst dimension stability. On the other hand, dimension stability test results of GRR and GBFFD decreased by 2.12% and 27.65%, respectively when compared to G (Figure 1). The RWA compound solves a small amount at the 70 °C temperature. In this case is the quantity of the dimension stability is increased. Due to the compound of organic GRH structure is the solvation resistance strong. In this occasion is the changing of the dimension stability minimum in these materials.

Tensile test was conducted according to ISO 37 norm. Empirical test results showed that tensile strength was 10.2 MPa in G compound. However, failure strength of GRR compound in new filling materials had the highest tensile strength (4.7 MPa) and GBFFD compound had the lowest tensile strength (2.5 MPa). %elongation values showed that %elongation of G was 420%. However, after the addition of new filling materials, GRR had a %elongation of 332% and GBFFD had %elongation value of 180% (Figure 2). The aggregation leads to the formation of weak point in the NR matrix, accordingly reduces the elastomeric strength.<sup>19,20</sup>

Relative volume loss (wearing) test results were conducted according to ISO 4649 standard. It was observed that wearing levels of G, GRH and GRR were 217, 282 and 203 mm<sup>3</sup> respectively. According to international ratios, wearing amount should be maximum 250 mm<sup>3</sup>.

Hardness test results were conducted according to ISO 868

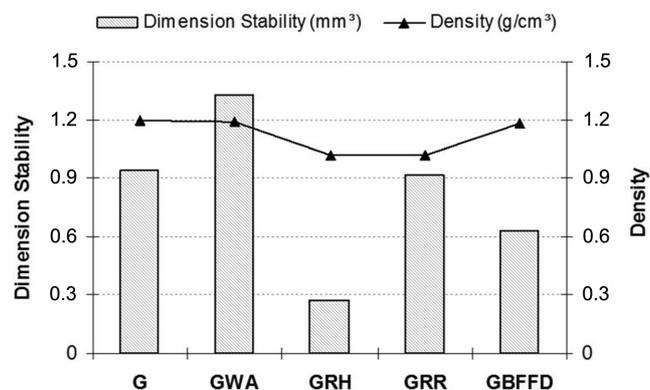


Figure 1. Dimension stability and density of general and new filling material compounds.

norm. It was observed that the hardness of G compound was 65 Shore A. The lowest hardness value was observed in GRR (55 Shore A), while the highest hardness value was observed in GRH 62 Shore A (Figure 3). As a mentioned, the hardness of silica increased in the elastomer based type rubber materials. In the new compounds is silica unused. Due to the new compounds hardness is in compares with the compound of G hardness has been lower observed. As expected in this study was the hardness strength lower. In a other study is the hardness strength decreased by use of 40% filler material.<sup>21,22</sup>

Tearing test results were conducted according to ISO 34 standard. It was found that G had a tearing value of 11.3 kN/m. On the other hand, among the new compounds, GRH had the highest tearing value (4.6 kN/m), while GWA had the lowest tearing value (3.2 kN/m). Addition of the new filling materials in the NR/SBR compound lowered the degree of crosslinks. The dimension force is known to be dependent on the contents of the crosslink density.<sup>23</sup> The rate of crosslink in the new filling materials may reduce. Due to the force of the tearing decrease. According to the original compounds is the

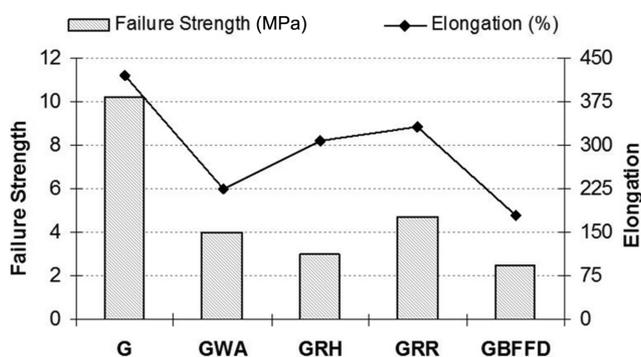


Figure 2. Elongation and failure strength of general and new compounds test parts.

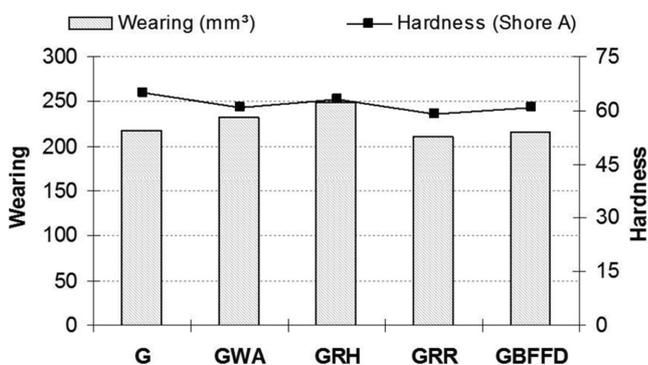
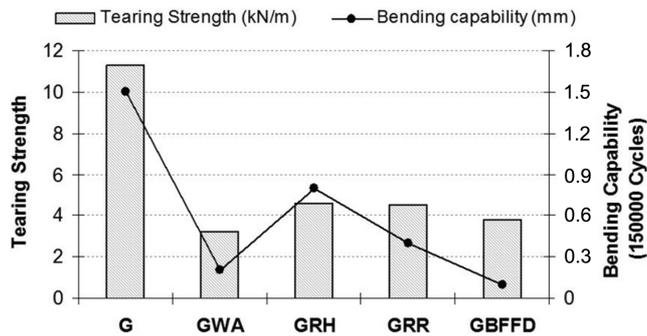


Figure 3. Wearing and hardness of general and new filling material compounds.



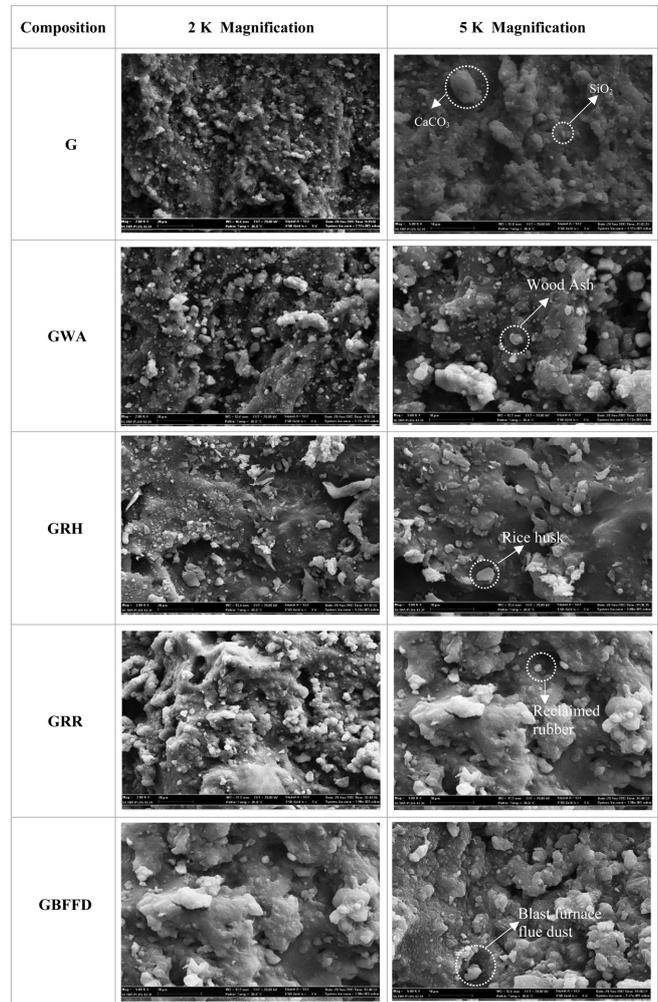
**Figure 4.** Tearing strength and bending capability of general and new filling material compounds.

tearing strength weak because the filler material with matrix materials are not crosslinked.<sup>24,25</sup> Ross-Flex type bending test was carried out in accordance with ISO 4643 norm. A total of 30.000 steps were taken in bending test; however the material showed no change. Thus, number of steps was increased to 100.000 and then to 150.000. Test results showed that notch enlargement value in G compound was 1.5 mm. As for the new formulae, GRH showed a highest enlargement (0.8 mm), while GBFFD showed the lowest enlargement (0.1 mm) as indicated in Figure 4. In an other study, shows that the value of bending from the filling materials are negatively affected.<sup>26</sup> But in this study observed the values of bending was positively affected. The elasticity modulus of the used falling materials rises is considered. In this case is considered a positive effect of strutting test.

SEM (scanning electron microscope) images of the specimens were taken. SEM images of the specimens in Figure 5 show the distribution of filling materials in rubber matrix and worn surfaces. Worn surfaces of the specimens which were subjected to wearing tests were coated with 100% gold and SEM images were taken. It is understood from Figure 5 that G, GWA, GRH, GRR and GBFFD specimens had different images and that physical properties of the used filling materials were visible from SEM images.

## Conclusions

Test results showed that (Table 3) new filling materials which replaced  $\text{SiO}_2$  and  $\text{CaCO}_3$  reduced density. The lower density values are, the lighter the shoe sole will be as the volume will remain unchanged. Hardness value slightly decreased when compared to G compound. Wearing resistance increased in GWA and GRH, however decreased in GRR and GBFFD



**Figure 5.** Worn surface of general and new compositions specimen.

when compared to G. %Elongation value of G compound was found to be higher than those of new compounds which were produced by using new filling materials. However, since GWA, GWA and GRR compounds are above the international standard does not possess a problem. On the other hand GBFFD was slightly below the international standard. It was found that failure strength and tearing strength of new compounds were lower than those of G compound. As for bending capability test results, initially 2 mm hole showed an enlargement of 1.5 mm in G compound; however this enlargement was much smaller in new compounds. Dimensional stability test results showed that G compound showed  $0.94 \text{ mm}^3$  deformation. Deformation was found to increase in GWA compound and to decrease in GRH, GRR and GBFFD compounds.

SEM images reveal that wood ash (GWA), reclaimed rubber (GRR) and blast furnace flue dust (GBFFD) showed a good

**Table 3. Physical and Mechanical Properties of General and New Compounds**

Physical and mechanical properties	Standard values (IS 5676 )	G (General compound)	GWA	GRR	GRH	GBFFD
Density (g/cm <sup>3</sup> )	Max. 1.5	1.2	1.19	1.02	1.02	1.18
Hardness (shore A)	Min. 55	65	57	62	55	57
Wearing	Max. 250	217	245	282	203	216
% Elongation	Min. 200	420	225	307	332	180
Failure strength	Min. 5.8 MPa	10.2	4	3	4.7	2.5
Tearing strength	Min. 6 kg/mm <sup>2</sup>	11.3	3.2	4.6	4.5	3.8
Bending capability (150000 cycles)	Max. 6	1.5	0.2	0.8	0.4	0.1
Dimensional stability (mm <sup>3</sup> )	-	0.94	1.33	0.27	0.92	0.63

and homogenous distribution in NR/SBR matrix. No failure or tearing occurred during wearing. Excluding rice husk, grain size of the used filling materials are approximately 10 microns. Due to its hard structure, desired grain size values could not be achieved in rice husk. As indicated in SEM images, as filling materials that used rice husk (GRH) did not have the same size, a homogenous mixture could not be obtained. This had a negative impact on mechanical properties.

Based on these results, excluding their tearing and tensile strength properties, GWA and GRR compounds can be considered as good shoe sole compounds when compared to G compound. On the other hand, GRH and GBFFD compounds can be considered to have the same quality with G compound; their mechanical properties are compatible with or slightly below international standards. They have lower density than G compound. The expectations from shoe soles vary according to the location where they will be used, functions of use and climate conditions.

Test results and SEM images showed that wood ash, reclaimed rubber, rice husk and blast furnace flue dust can be used as filling materials in NR/SBR type elastomer materials. Varying ratios of wood ash, rice husk, blast furnace flue dust and reclaimed rubber materials can be added to general compound without removing SiO<sub>2</sub> and CaCO<sub>3</sub>.

It is hard to fragment rice husk, which is not a recyclable material, due to its hard structure. Rice husk can be used in NR/SBR type rubber shoe soles by furnacing and adding their dust.

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