

# Development and Characterization of Nitrosamine-Free Rubber Compounds Using Bio-Based Ethylene-Propylene-Diene Rubber

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**Abstract-** This study investigates the effect of white fillers such as silica, talc and kaolin (loading 60-100 phr) on rheological, mechanical and thermal stability of bio-based ethylene-propylene diene (EPDM) rubber compounds. Rheological properties such as minimum (ML) and maximum torque (MH), scorch time (ts2) and optimum cure time (t90) was estimated by moving die rheometer. Mechanical properties such as tensile strength, elongation at break, hardness and tear strength were measured at room temperature. Process and low temperature behavior of compounds were simulated by using rubber process analyzer machine with strain sweep and frequency sweep analyses, respectively. From obtained results, silica loaded compounds showed higher ML and MH values, but vulcanization efficiency was the highest on the compounds included kaolin filler. Kaolin and talc fillers increased the tensile strength of the compounds, silica increased the hardness value of compounds. Also, kaolin has good barrier property against to heat aging. The change of tensile strength and elongation at break values of silica loaded compounds increased with silica incorporation.

**Keywords –** Elastomer; nitrosamine; renewable; sustainability; EPDM

## I. INTRODUCTION

Consumption of petrochemical-based polymeric materials increases their effects on the environmental and human health day by day. Polymeric materials form an important part of our daily life in parallel with the development of their properties. Petroleum, one of the natural resources, has a limited reserve like other non-renewable natural resources and also reducing production and negative effects of petrochemical-based materials after consumption has become one of the most crucial requirements of a more sustainable life. Nowadays, it is aimed to reduce the dependence on petroleum resources by increasing the use of materials obtained from renewable resources. So, the reduction of carbon footprint that will occur during the production of such products will enable future generations to live in a healthier world. The production and consumption of petroleum-based products which increase in parallel with the increase in the world population, reveals the necessity to reduce the use of products harmful to both the environment and human health. As a result of these concerns, academic studies have gained momentum in replacing petroleum-based and non-renewable materials with environmentally friendly materials obtained from renewable resources.

Due to their unique elastomeric properties, elastomers take their place in the literature as an important material class. They have a very wide usage area in our daily life as well as in defense, industrial, vibration damping, hose, space industry, especially in the tire industry. According to the Elastomers Market Research Report, 27 million metric tons of elastomers were consumed worldwide in 2020 and this number is increasing day by day. In addition to all these, the main building blocks of synthetic rubbers such as butadiene, isoprene are generally produced from crude oil. As a result, the elastomer industry is a major consumer of energy and raw materials, as well as generating large amounts of waste [1]. It should come as no surprise that the focus of scientific research has been to replace petroleum-derived twins with polymer materials derived from renewable resources such as biomass, that provides remarkable reduction in carbon footprint and dependence on petroleum-based sources [2]. This strategy has been already started to use for thermoplastics [3, 4, 5, 6, 7],

Some bio-elastomers having potential use in tissue engineering, drug delivery and in vivo sensing, reported [8, 9, 10, 11, 12]. However, the monomers in these studies were not required to be derived from biomass – they just had to

be biocompatible, with degradation products which were nontoxic to human bodies. Also, the mechanical and physical properties (such as tensile strength) of these materials are not suitable for engineering applications [1]. However, in the beginning of 2011, ARLANXEO announced production of bio-based EPDM called as “Keltan ECO” rubber which has up to 70 percent bio-based content. The used ethylene is derived from ethanol produced from sugarcane. Regular EPDM products are produced from fossil raw materials, the ethylene and propylene are produced via cracking of natural oil. Bio-based EPDM is a recent ARLANXEO’s development, produced from bio-based ethylene. Keltan ECO is produced in the ARLANXEO’s EPDM plant in Triunfo, Brazil, by means of a solution polymerization process using Ziegler Natta catalyst technology. Depending on the ethylene content of the particular grade, the bio-based content of Keltan EPDM rubber ranges between 50 and 70 wt% [13].

Generally, rubber products include fillers, plasticizers and also need crosslinking agents and accelerators for vulcanization. Dithiocarbamates, sulfenamides, thiurams and some sulfur donor accelerator which are widely used accelerators form secondary amines that are nitrosatable by oxides of nitrogen when they break down. Magee and Barnes (1967) reported that dimethyl nitrosamine is a serious carcinogen in laboratory animals [14]. Amines are chemical compounds derived from ammonia (NH<sub>3</sub>). Primary, secondary and tertiary amines are created by substituting hydrogen (H) in ammonia with a carbon-containing group (-R). The substitution of two hydrogen atoms with two carbon-containing groups produces secondary amines. Nitrosamines (NA) are composed by secondary amines reacting with oxides of nitrogen. NAs are occurred generally through the vulcanization and/or post-curing period. During these process NAs can be mixed with air and taken into the human body by breathing. Also, NAs can come to the surface on rubber during storage and service. Therefore, the most common exposure routes, especially in the rubber industry, are inhalation and dermal contact. For several years, Germany has led the effort to eliminate the use of common nitrosamines in the rubber industry. Their TRGS 522(Nov 95) allows no more than 2.5 µg/m<sup>3</sup> emission of nitrosamines between vulcanization and warehousing. Additionally, major U.S. Automobile manufacturers have issued stringent requirements with regards to the use of nitrosamines. One company has issued a restricted substances standard that prohibits the use of nitrosamines in excess of the 0.1% threshold value of the part’s total weight. With over 300 nitrosamines listed as either known or suspected carcinogens, safety continues to drive the elimination of nitrosamines in the rubber industry. After 1980s, as test equipment that was able capable to detect the impact of nitrosamine, more than 90% of the 300 nitrosamines have been classified as either a carcinogen or a mutagen [15]. However, the application of zinc dithiophosphates (ZBOP) as either accelerators or sulphur donors during diene rubber vulcanization has been well established for many years [16, 17, 18] as nitrosamine free accelerators.

In this study, effects of common white fillers which are consumed in rubber industry such as talc, kaolin and precipitated silica have been investigated on physical, mechanical, and aging properties of bio-based EPDM rubber compounds which are formulated as nitrosamine-free vulcanization systems. Aging media is selected as heat to analyze which effects the fillers show on properties.

## II. MATERIALS AND METHODS

### A. Materials

Bio-based EPDM rubber, Keltan Eco 5470 was supplied from Arlanxco Rubber company, Mooney viscosity 55 MU, ethylene content 70%, ENB content 4.6%, specific gravity 0,86. Carbon black, N326 was supplied from BIRLA Carbon company. Silica (surface area, 175 m<sup>2</sup>/g), kaolin (hydrated aluminum silicate) (surface area, 8 m<sup>2</sup>/g), and talc (surface area, 23,62 m<sup>2</sup>/g), fillers were supplied from Evonik Degussa GmbH, Imerys Minerals Ltd and Egemin Madencilik, respectively. Zinc dialkyldithiophosphate (ZBOP) was supplied from Lanxess Rhein Chemie.

### B. Methods

Formulation of the composites is given in Table I. The rubber compounds were prepared in the lab-scale open mill. First, EPDM rubber was plasticated for 7 minutes and subsequently filler and plasticizer were introduced and mixed for 10 minutes then other chemicals were added and mix for 10 minutes. After that, the compounds were homogenized.

Table I: Formulation of compounds

Sample	Compounds (phr <sup>a</sup> )										
	EPDM	Pre. Silica	Kaolin	Talc	CB	Plasticizer	ZnO	Stearik Asit	ZBOP <sup>b</sup>	MBT <sup>c</sup>	Sulphur
SIL60	100	60	-	-	80	80	5	1	0.5	0.5	1.5
SIL80	100	80	-	-	80	80	5	1	0.5	0.5	1.5
SIL100	100	100	-	-	80	80	5	1	0.5	0.5	1.5
KAO60	100	-	60	-	80	80	5	1	0.5	0.5	1.5
KAO80	100	-	80	-	80	80	5	1	0.5	0.5	1.5
KAO100	100	-	100	-	80	80	5	1	0.5	0.5	1.5
TAL60	100	-	-	60	80	80	5	1	0.5	0.5	1.5
TAL80	100	-	-	80	80	80	5	1	0.5	0.5	1.5
TAL100	100	-	-	100	80	80	5	1	0.5	0.5	1.5

<sup>a</sup>: per hundred rubber  
<sup>b</sup>: zinc dialkyldithiophosphate  
<sup>c</sup>: 2-Mercaptobenzothiazole

The curing characteristics were investigated from corresponding curing isotherms measured by the ALPHA MDR 2000 at 185 oC and viscosity values were obtained by ALPHA MV 200 at 100 oC. Also, strain and frequency sweep analyses were performed by using ALPHA RPA 2000 at 100 oC for simulating process conditions. Frequency 0.5 Hz, temperature 100oC, preheating for 4 minutes and strain between 0.7% and 1000% were selected in RPA Strain sweep tests. In frequency sweep tests, 2.8% strain, 100oC temperature, 4 minutes preheating were applied and tests between 0.03 and 50 Hz were performed.

The test specimens were cured at 150 oC and 90 bar by using suitable molds considering their rheological values. The vulcanization times were determined as follows; 30' for 2 mm plates, 45' for abrasion samples, 60' for compression set test specimens.

The tensile properties of tested vulcanizates were measured by using the Zwick/Roell Z020 at cross-head speed of 500 mm/min at laboratory temperature, in accordance with ISO 37 standard; tear test was performed at 500 mm/min for angle type test specimens, in accordance with ISO 34-1 standard.

Heat aging tests were performed for 168 hours at 100 oC, in accordance with ISO 188 standard.

### III. EXPERIMENT AND RESULT

#### A. Rheometric Characteristics

Table II show the rheometric characteristics, such as the minimum and maximum torque, delta torque, scorch time (ts2) and optimum cure time (t90). The ML value can be taken as a parameter showing the filler-filler interactions before curing [19, 20]. However, the low ML value of kaolin and talc, which have weaker bonds between their particles, can be explained by the low surface area, electrically neutral surface, and the very low density. Due to this feature of kaolin and talc, it is especially preferred in the process of compounds containing very high filling and high viscosity such as EPDM mixtures. Also, the scorch time (ts2) was dramatically prolonged with the use of kaolin and talc compared to the same amount of silica content; this has shown that process safety and machinability have increased. In other words, with this extended period, production efficiency can be improved for stages such as mixing, milling, molding and filling the mold in injection.

Table II: Rheometric characteristics of compounds

Sample	M <sub>L</sub> , dNm	M <sub>H</sub> , dNm	M <sub>H</sub> -M <sub>L</sub> , dNm	t <sub>s2</sub> , min	t <sub>90</sub> , min	Vis, MU
SIL60	4.93	13.92	8.99	0.94	6.22	103

SIL80	9.92	17.35	7.42	0.93	4.51	152
SIL100	17.90	23.35	5.45	1.52	4.25	199
KAO60	0.72	10.03	9.31	1.16	7.42	28
KAO80	0.86	10.42	9.57	1.13	7.46	30
KAO100	0.92	10.77	9.84	1.1	7.53	32
TAL60	0.86	9.46	8.60	1.29	7.31	29
TAL80	0.93	8.34	7.41	1.46	7.44	30
TAL100	0.98	7.63	6.64	1.61	7.72	31

Viscosity value, which was 103 MU in the presence of 60 phr silica, showed a significant increase, reaching 152 and 199 MU values with silica content of 80 and 100, respectively. However, while the viscosity value of the compound containing 60 phr kaolin was 28 MU; 30 and 32 MU values were measured as at 20 and 40 phr increments, respectively. A similar situation is valid for compounds containing talc, where the viscosity value of 28.6 MU in compound containing 60 phr talc showed a negligible increase by showing 30 and 30.6 MU at 80 and 100 phr loadings, respectively.

When the MH values, which are indirectly related to the crosslink density after vulcanization, are examined, it is observed that the MH values increase significantly with the increase in the silica content. Since the structure of kaolin and talc is in layers, this structure can be attached to large polymer chains in two dimensions. However, since the diameter of this layered structure remains too large, it has a very weak bonding strength with the polymer matrix. The spherical structure of silica allows the particles to interact more strongly with the polymer chains in three dimensions, while the high surface area supports them to form more bonds.

It was observed that while the MH-ML value decreased with the amount of silica, it did not significantly change with the amount of kaolin and talc. Based on this result, it can be said that the -OH groups on the silica surface adsorb the catalysts during curing and reduce the amount of crosslinking. Increasing  $t_{s2}$  and decreasing  $t_{90}$  values also support this situation. The use of silica bonding agents, silane, etc., is recommended when using high amounts of silica.

#### B. Strain Sweep Analyses

The effect of white filler type and amount on Shear Modulus ( $G'$ ) and  $\tan\delta$  values at different strains is given in Figure 1 and Figure 2. It has been observed that there is a linear viscoelastic region at low strains in the raw polymer, in which the storage modulus of the material is independent of shear strain. However, although the storage modulus increased with the addition of silica, the linear viscoelastic region did not disappear. With the addition of kaolin, the initial storage modulus decreased but increased with increasing shear strain and decreased at high strains with weakening of the filler-fill interactions.

However, with the replacement of the filler type with kaolin or talc, the linear viscoelastic region disappeared, and lower  $G'$  values were obtained compared to the silica-containing mixtures at low strains. Viscosity and ML values of the mixtures also support these results.  $G'$  values increased with increasing strain amount. This can be interpreted as an indication that talc and kaolin structures make chain mobility difficult at increasing strains.

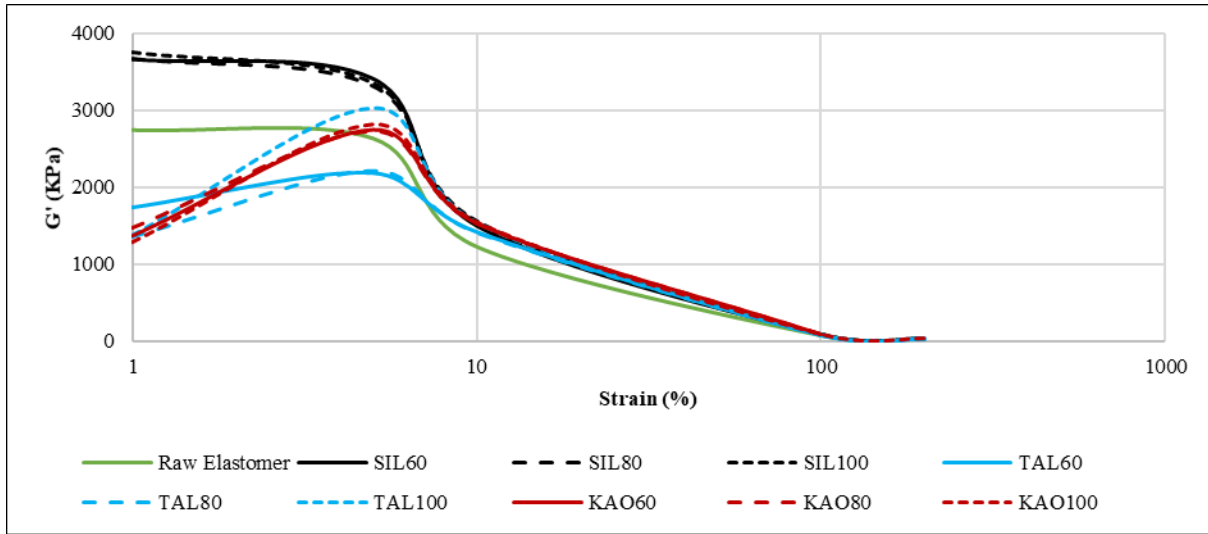


Figure 1: The effect of white filler type and amount on  $G'$  on strain sweep

Considering the  $\tan\delta$  values, the values increased due to the increased shear strain due to the bulky and layered structure of kaolin and talc that limits the chain movements. The increase in  $G'$  values also confirms this result. The overlap of  $G'$  and  $\tan\delta$  values of all compounds and raw polymer at increasing strain values can be interpreted as an indication that they will show similar behavior during the process.

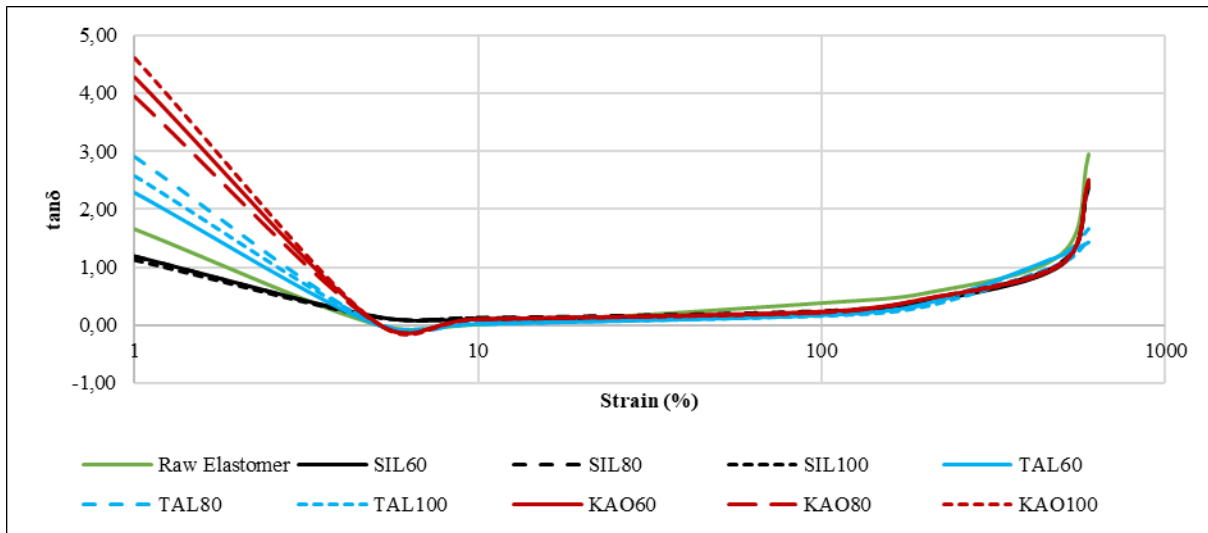


Figure 2: The effect of white filler type and amount on  $\tan\delta$  on strain sweep

### C. Frequency Sweep Analyses

Considering the decreasing chain mobility, the behavior at high frequency values is thought to be similar to that at low temperatures. Figure 3 and Figure 4 show the absence of dramatic changes in  $G'$  and  $\tan\delta$  values at high and low frequencies indicates that the behavior of raw polymers and blends is weakly dependent on time.

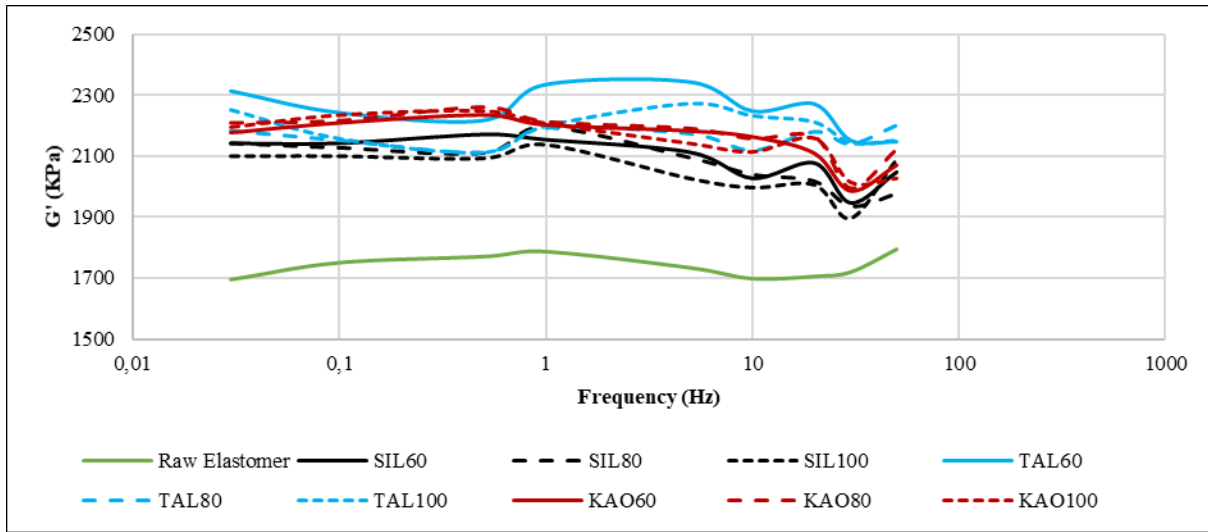


Figure 3: The effect of white filler type and amount on  $G'$  on frequency sweep

It was observed that the addition of fillers increased the  $G'$  values compared to the raw polymer. This shows that the mobility of the polymer chains decreased as expected. However, the higher  $G'$  value of the talc addition at high frequencies indicates that the structure will be harder at low temperatures compared to silica and kaolin.

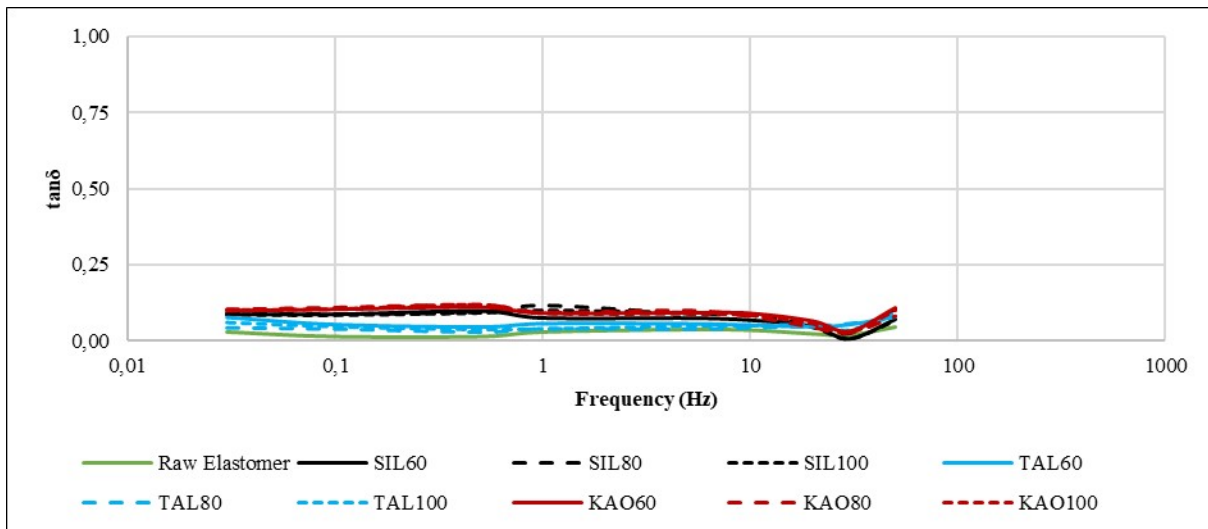


Figure 4: The effect of white filler type and amount on  $\tan\delta$  on frequency sweep

#### D. Mechanical Properties

The effects of white filler type and amount on tensile strength, elongation at break, hardness and tear strength properties are given in Figure 5, Figure 6, Figure 7, Figure 8, respectively. As can be seen in Figure 5, the tensile strength values decrease with the increase in the amount of white filler. Contrary to carbon black, the decrease in tensile strength with the amount of white filler confirms the result that carbon black forms physical crosslinking due to its structure.

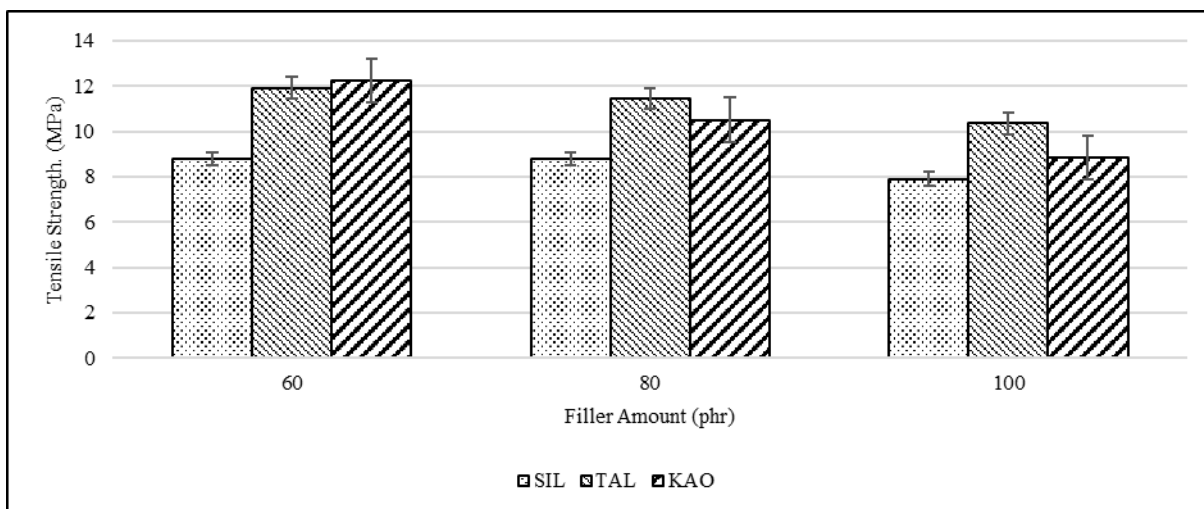


Figure 5: The effect of white filler type and amount on tensile strength of compounds

When the effects of the fillings at the same rates are considered, it is seen that the strengths of the compounds containing talc are higher when compared to the other two filling types. In other words, as mentioned above, -OH groups adsorb catalysts on the surface of silica, reducing the cross-link efficiency, which leads to weakening of inter-chain bonds. These results are supported by reductions in elongation and tear strength (Fig. 6 and Fig. 8). Another reason for the decrease in strength values with the increase in the amount of filler is explained by the formation of deagglomeration with the excessive increase in the amount of filler [21].

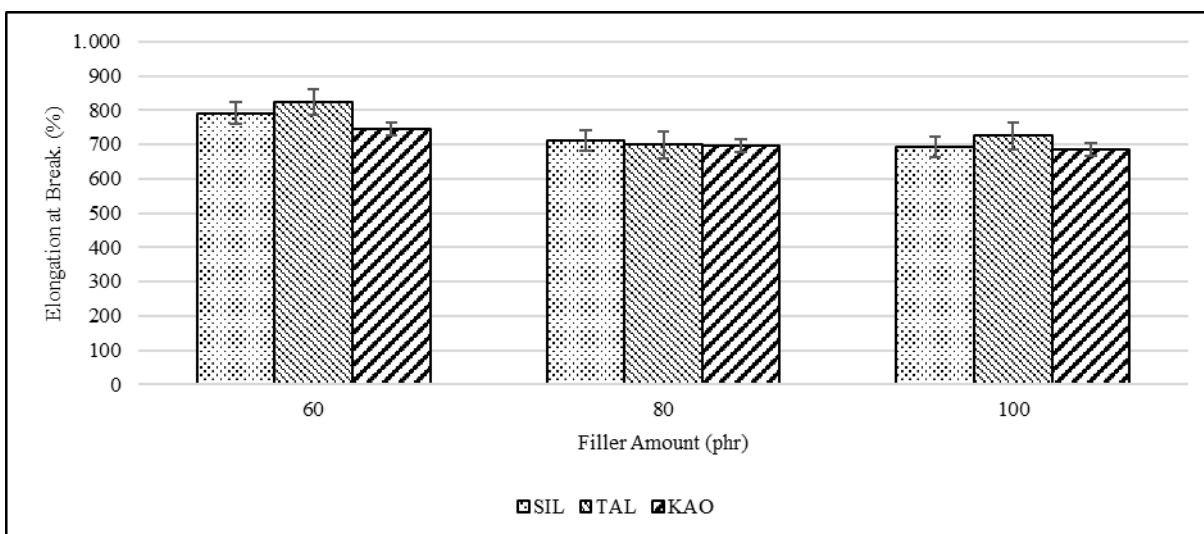


Figure 6: The effect of white filler type and amount on elongation at break values of compounds

Due to the mineral structure of white fillings, in other words, their non-elastic nature, they increase the hardness values. When silica and kaolin and talc are compared, it is seen that silica enters between the polymer chains and makes the structure more rigid.

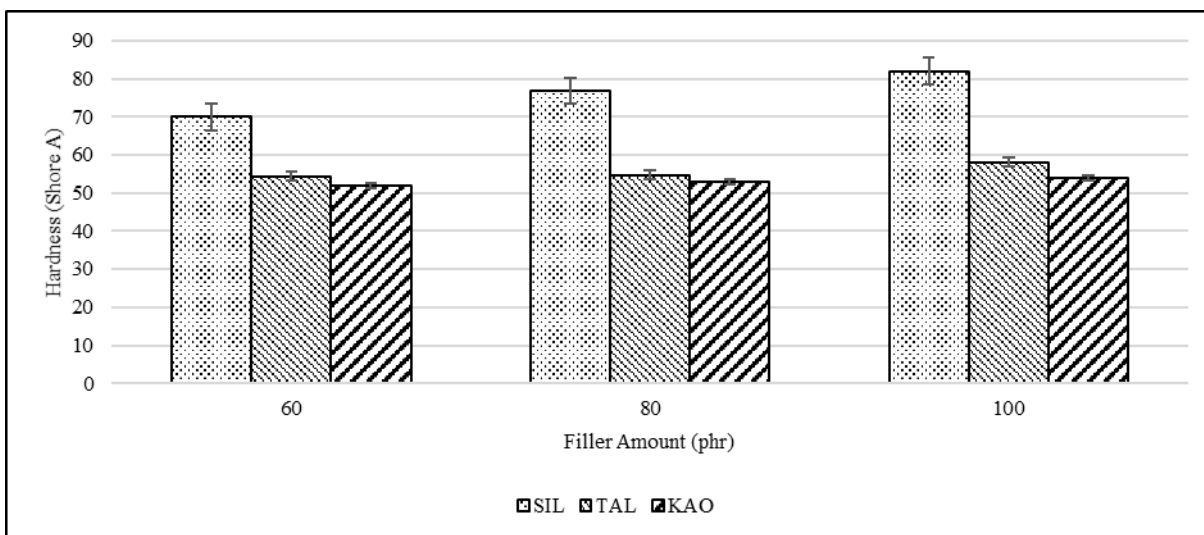


Figure 7: The effect of white filler type and amount on hardness values of compounds

On the tear strength results, increasing the amount of kaolin up to the optimum level of 80 phr increased the tear strength, while increasing it after this level caused the values to decrease. When kaolin and talc and silica are compared in the same ratios, as mentioned above, it has been observed that the tear strength of the compounds containing silica, which is thought to have low crosslink density, is also low. In addition, it is seen that kaolin and talc fillers increase the tear strength compared to the silica-containing compounds, since they reduce the chain mobility and take the applied force on them.

#### E. Aging Properties

Aging test were performed under heat at 100 oC for 168 hours in oven. Effect of filler type and amount on tensile strength, elongation at break, hardness and tear strength change after aging were given in Table III. The values in the figures give the change after aging as percent compared to the values before aging.

It is seen that the tensile strength value after thermal aging increases as the silica content of the compounds. This can be interpreted as an indication that the crosslink density increases during aging in compounds containing silica. However, due to the layered structures of talc and kaolin, they act as a barrier during aging and reduces the change in tensile strength, elongation and tearing values after aging.

Table III: Aging properties of compounds

	SIL60	SIL80	SIL100	KA060	KA080	KA0100	TAL60	TAL80	TAL100
Tensile Str. Change, %	11.14	19.48	30.51	11.73	10.60	10.67	12.89	31.44	34.97
E@B Change, %of%	-44.59	-50.63	-54.50	-32.27	-35.40	-35.53	-45.58	-34.44	-36.50
Hardness Change Sh A	5.00	3.00	3.00	5.50	6.67	6.67	7.83	10.00	8.67
Tear Str. Change., %	-43.44	-59.86	-60.94	-15.67	-20.03	-4.50	-14.63	-8.57	2.48

#### IV.CONCLUSION

Minimum, maximum torques (MH and ML) and viscosity values of compounds increased with silica incorporation and were not affected by talc and kaolin loading. Although increasing MH values, MH-ML values decreased by silica, this can be considered as increasing silica incorporation reduced cross-link density, therefore reduced vulcanization efficiency. Talc and kaolin do not have significant effect on rheological properties. The storage modulus increased with silica; the initial storage modulus decreased with the addition of kaolin. Talc increased tensile strength of compound after 80 phr when compared other two fillers. All types of filler load decreased



elongation at break values due to their non-elastic behavior. Silica increased hardness values of compound due to its higher surface area. The compound included talc showed good tear strength values. Changes after aging show kaolin has good barrier property against to heat aging. The change of tensile strength and elongation at break values of silica loaded compounds increased with silica incorporation. These characterized compounds can be used in places where high ozone and UV resistance is required, in fast consumption products, in industrial water and cooling water transport systems, provided that they are subjected to the relevant regulation tests, in products that may come into contact with food.

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