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Farklı Etilen Oranlarına Sahip EPDM Kauçuklarından Kükürt Vulkanizasyonuyla Üretilen Kauçukların Reolojik ve Mekanik Özelliklerinin İncelenmesi

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ÖZET

Bu çalışmada, etilenin kauçukların reolojik ve mekanik özellikleri üzerindeki etkisi araştırılmıştır. Bu amaçla farklı oranlarda etilen içeren EPDM kauçukların karıştırılması ve kükürtle kürlenmesi ile kauçuklar üretilmiştir. Formülasyonlar, tüm numunelerin aynı sertliğe sahip olması için modifiye edilmiştir. Reometre analizi sonuçları, Suprene 512 F numunesinin maksimum kür torkunun (M/dN.m) diğer iki numuneden daha yüksek olduğunu, ancak kür süresinin %90'ının diğer iki numuneden daha geç olduğunu ortaya koymuştur. Çekme-uzama analizi, en yüksek etilen içeriğine sahip Suprene 512 F kauçuğunun Ts/MPa ve Eb/% oranlarının daha yüksek olduğunu ortaya koymuştur. Sertlik analizi, kauçuktaki etilen miktarındaki artışın, çekme kopma mukavemetindeki artışla doğru orantılı olduğunu ortaya koymuştur. Ayrıca kauçuktaki etilen oranının vulkanizasyon sonrası sertlik değişimini lineer olarak etkilediği görülmüştür. Kauçuk karışım formülasyonları yapılırken karışımdaki etilen oranının vulkanizasyon sonucu oluşan ürünün sertliğinde meydana gelen değişimi doğrudan etkileyeceği göz önünde bulundurulmalıdır.

Investigation of Rheological and Mechanical Properties of Rubbers Produced by Sulfur Vulcanization from EPDM Rubbers with Different Ethylene Ratios

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ABSTRACT

In this study, the effect of ethylene on the rheological and mechanical properties of rubbers was investigated. For this purpose, rubbers were produced by mixing EPDM rubbers containing ethylene in different ratios and curing with sulfur. The formulations were modified so that all samples had the same hardness. The results of the rheometer analysis revealed that the maximum cure torque (M/dN.m) of the Suprene 512 F sample was higher than the other two samples; however, 90% of the curing time was later than the other two samples. Tensile-elongation analysis revealed that the Ts/MPa and Eb/% ratios of Suprene 512 F rubber with the highest ethylene content were higher. The hardness analysis revealed that the increase in the amount of ethylene in the rubber was directly proportional to the increase in the tensile breaking strength. In addition, it was observed that the ethylene ratio in rubber linearly affected the hardness change after vulcanization. While making rubber blend formulations, it should be considered that the ethylene ratio in the mixture will directly affect the change in the hardness of the product formed as a result of vulcanization.

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Introduction

Ethylene Propylene Diene Rubber (EPDM), a very important synthetic rubber in the industrial field, has very good heat, UV light, oxygen, and ozone resistance and has a saturated polymer backbone (Spanos et al. 2014). Specifically, EPDM rubber is used in automotive sealing gaskets (window, door, and body), o-rings, waterproof gaskets for joining tunnel segments, roofing gaskets for building constructions, etc; therefore, it has become one of the most widely used sealing elements in industry (Da Maia et al. 2013; Pourmand et al. 2016; Li et al. 2019; Tu et al. 2021). EPDM is a rubber with excellent elasticity, low temperature flexibility, and good electrical insulation properties due to its non-polar and saturated hydrocarbon backbone structure. In addition to these important features that are preferred in industrial applications, it has superior resistance to heat, oxygen, ozone, and UV. EPDM elastomers can vary according to the amount and type of diene used, as well as in different ethylene and propylene ratios (Brydson, 1978). The quantitative ratio of monomers gives the elastomer certain properties (Wheelan and Lee, 1981), such as the production of high green, strong polymers when high ethylene content is used. Ethylene content used at low and medium values produce softer and more elastic polymers. The higher the ethylene content, the more likely the polymer to get filler, and the better mixing and extrusion process (Abdou-Sabet and Fath, 1982). EPDM rubber products can be used as a supporting product in high cost parts in different usage areas of the industry. The change in the microstructure of rubbers brings about general structural effects, and as a result, these structural deteriorations can affect the degradation properties of the composites used with EPDM rubber mixture (Kole et al. 1993; Gamlin et al. 2011). Choosing rubber with the wrong ethylene ratio while making rubber mixture formulations may cause the risk of hardness change of the product at low temperatures, and financial losses in the materials or structures used together. Therefore, this effect should be taken into account when creating formulations and should be controlled with process parameters.

The aim of this study is to investigate the effect of the ethylene ratio in the rubber raw material on the rheological and mechanical properties of Dutral TER 4049 and Suprene 512F EPDM rubbers mixed at different rates after curing with sulfur.

Material and Methods

Materials

The EPDM rubber materials used in this study are Dutral TER 4049 produced by Universal, and Suprene 512 F produced by SK Global Chemical, and their properties are shown in Table 1.

Table 1. EPDM rubber properties.

Grade	Diene content ENB (%)	Ethylene content	Mooney (ML 1+4 125 °C) (MU)	Extender oil paraffinic (phr)
Dutral TER 4049	4.5	60	76	-
Suprene 512 F	4.5	69	63	-

The following additives are added to the mixture during rubber preparation. These are

- Carbon FEF N 550 (Omsk Carbon Group) and Pro 1500 (Alkim Petro Kimya) as fillers
- 1618RG Stearic acid and ZnO (Melos A.Ş.) as activators
- AFLUX 42 and PEG 4000 as process facilitators
- TMTD, MBTS, and CBS from Eigenmann & Veronelli as accelerators
- Sulfur as a vulcanization agent
- and Kezadol (80% CaO) from Kettlitzas moisture inhibitor

An industrial size Model X(S)N-110 Kneader was used to mix the rubber mixture. Model X(S)K800 was used as mill and Model XP-600 Batch off Cooler (Taixing Ruixing Rubber & plastic Machinery Co. Ltd.) was used as cooling machine. These machines constitute the machine park used in rubber production.

Formulations

Three different formulations were written by using two different types of EPDM rubber and the same hardness was adjusted in three formulations. Table 2 shows the content of rubbers in different formulations.

Table 2. Rubber mixtures prepared in different formulations (phr).

Content	Suprene 512 F	Suprene 512 F (%50)-Dutral TER 4049 (%50)	Dutral TER 4049
Rubber	100	100	100
Carbon (FEF N 550)	81.7	85	86.7
Paraffinic Oil	76.7	76.7	76.7
Active ZnO	6.7	6.7	6.7
Stearic Acid	2.5	2.5	2.5
AFLUX 42	2.0	2.0	2.0
PEG 4000	2.0	2.0	2.0
TMTD	1.17	1.17	1.17
MBTS	1.17	1.17	1.17
CBS	0.83	0.83	0.83
S	0.9	0.9	0.9
CaO	6.7	6.7	6.7

Methods

Preparation of EPDM blend mix

Three different formulations were prepared for this study. For each formulation prepared, the rubber raw material was chewed in a kneader machine at 90 °C for 1.5 min. Then, Carbon (FEF N 550), paraffinic oil, active zinc, stearic acid, AFLUX 42, and PEG 4000 were added into the kneader machine at the phr ratios determined in the formulation. The mixture was allowed to mix for 5.5 min. Then, the amount of activators (TMTD, MBTS, CBS) determined in the formulation were added and mixed for 3 more minutes. The mixture, which was mixed in the kneader machine for a total of 10 min, was transferred to the mill at 110 °C output temperature. The rubber mixture in the mill was aerated for 1 min and its temperature was reduced. A certain amount of sulfur was added to the rubber mixture in the mill, and the temperature was lowered. The rubber mixture, which was mixed in the mill for 1 min and 40 sec, was cut and started to be given to Batch off Cooler. Transfer of the entire rubber compound mixture from the mill to the Batch off Cooler took place in 2 min 34 sec. The mixture, which was mixed by rotating in a total of 5 min and 14 sec, was sent to Batch off Cooler as a 14 cm long and 2 cm thick strip. The rubber mixture, which was cooled in Batch off Cooler for 16 min, was left to rest for 6 h in a cold room at 16 °C.

Rheological Properties

The hardness and curing properties of the EPDM rubber mixture were investigated using the GLK3000-MDR Rheometer at the test temperature of 185 °C. At the same time, min torque (ML), max torque (MH), torque difference (MH-ML), scorch time, and curing time were determined.

Tensile Strength and Elongation at Break

The tensile-elongation tests, which were the mechanical properties of the prepared EPDM rubber mixtures, were examined with the GLK3000-T5 Tensile-Breaking device at 200 mm/min speed according to ISO 37. Machine parameters used when testing according to ISO 37 standard were as follows: speed: 200 mm/min; direction: move up; extension type: trace; and load average times: 3. Tensile strength (Ts/MPa) and elongation break (Eb/%) values of the sample were determined.

Hardness Properties

Different EPDM rubber mixtures prepared here were investigated according to ISO 48 using hardness discs vulcanized at 185 °C for 4 min and 12 sec. In addition, three discs from each of the samples made with 3 different mixtures were taken and kept in an oven for 24 h at -10 °C, and the effects of temperature changes on hardness were observed.

Results and Discussion

Tensile Analysis

The results of the tensile analysis of the formulation containing Dutral TER 4049 made with parameters are shown in Figure 1 and Table 3.

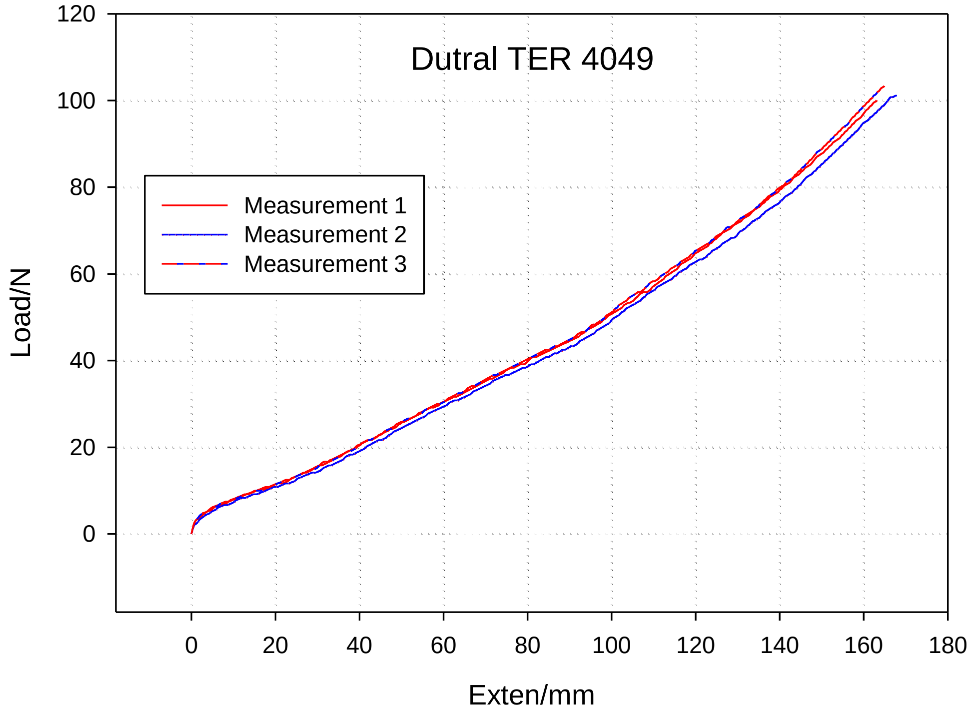

Figure 1. Tensile load of Dutral TER 4049.

Table 3. Tensile strength and elongation break analysis table for Dutral TER 4049 at different measurements.

Measurement	Thick/ mm	Width/ mm	Lo/ mm	Fmax /N	Lmax/ mm	Ts/M pa	Eb/ %	S50/ Mpa	S100/ Mpa	S200/ Mpa
1	1.95	4	25	72.78	171.62	9.33	686.5	0.7	1.1	2.37
2	1.95	4	25	80.56	178.9	10.33	715.6	0.8	1.23	2.52
3	1.95	4	25	84.17	176.64	10.79	706.6	0.91	1.39	2.78
A	1.95	4	25	79.17	175.72	10.15	702.9	0.8	1.24	2.56
V	0.00	0.0	0.0	5.82	3.73	0.75	14.9	0.11	0.15	0.21

The results of the tensile analysis of the formulation containing Suprene 512 F (50%) – Dutral TER 4049 (50%) made with the machine parameters are shown in Figure 2 and Table 4.

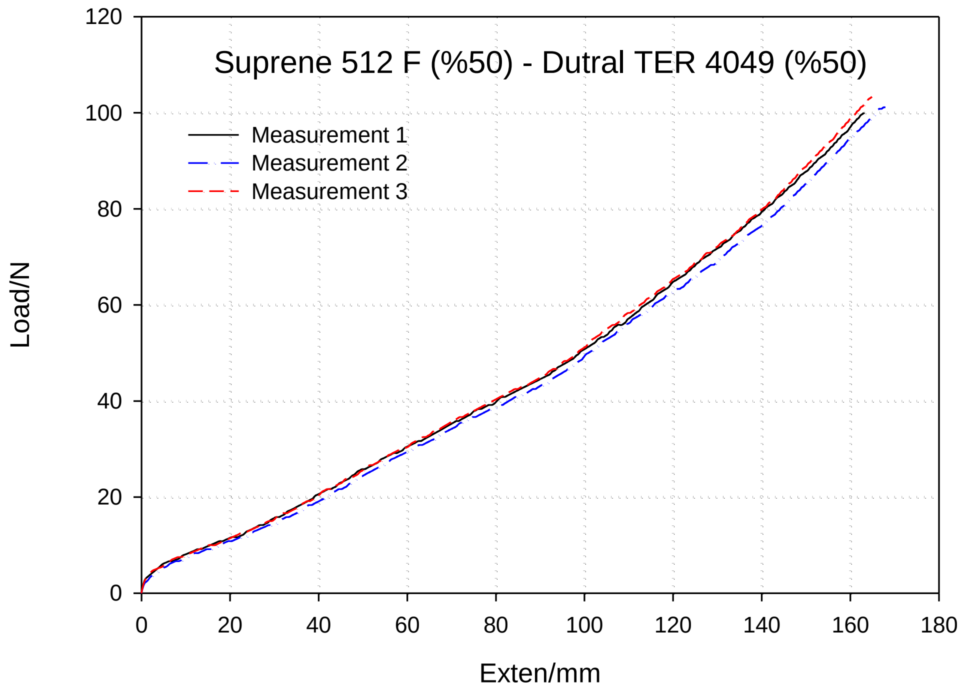

Figure 2. Tensile load of Suprene 512 F (%50) - Dutral TER 4049 (%50).

Table 4. Tensile strength and elongation break analysis table for Suprene 512 F (%50) - Dutral TER 4049 (%50) at different measurements.

Measurement	**Thick /mm**	**Width/ mm**	**Lo/ mm**	**Fmax/ N**	**Lmax/ mm**	**Ts/Mpa**	**Eb/%**	**S50/ Mpa**	**S100/ Mpa**	**S200/ Mpa**
1	1.95	4	25	89.72	158.62	11.5	634.5	1.1	1.67	3.26
2	1.95	4	25	95.00	165.68	12.18	662.7	1.07	1.67	3.24
3	1.95	4	25	78.61	145.59	10.08	582.4	1.05	1.62	3.2
A	1.95	4	25	87.78	156.63	11.25	626.5	1.07	1.65	3.23
V	0.00	0.00	0.0	8.37	10.19	1.07	40.8	0.03	0.03	0.03

The results of the tensile analysis using the ISO 37 standard for the formulation containing Suprene 512 F are shown in Figure 3 and Table 5.

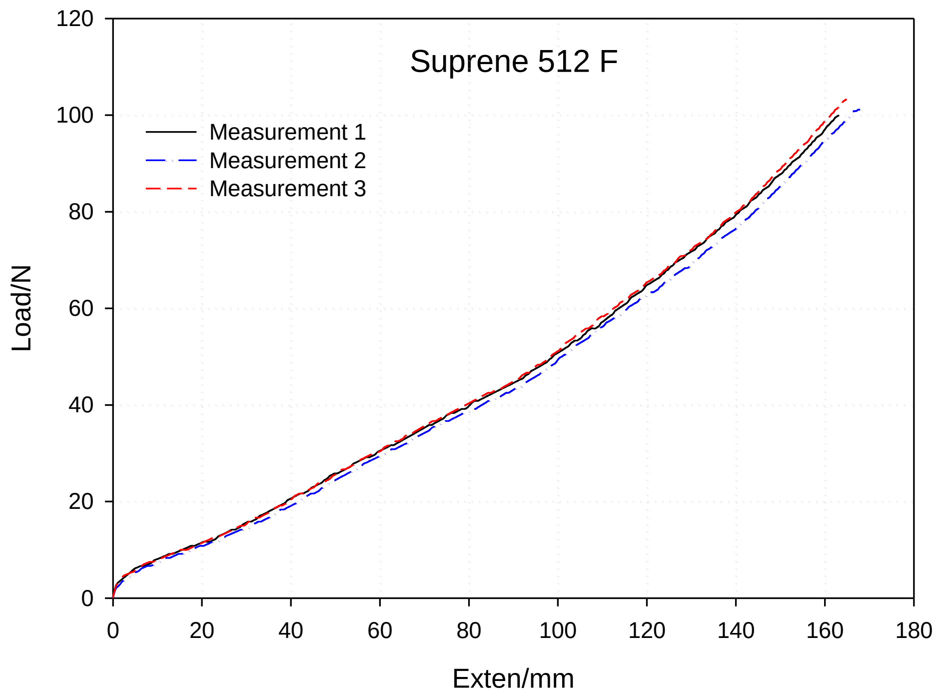

Figure 3. Tensile load of Suprene 512 F.

Table 5. Tensile strength and elongation break analysis table for different measurements of Suprene 512 F.

Measurement	**Thick /mm**	**Width/ mm**	**Lo/ mm**	**Fmax/ N**	**Lmax/ mm**	**Ts/Mpa**	**Eb/%**	**S50/ Mpa**	**S100/ Mpa**	**S200/ Mpa**
1	1.91	4	25	100	163.14	13.09	652.6	1.19	1.75	3.38
2	1.93	4	25	101.1	167.49	13.1	670.0	1.08	1.63	3.17
3	1.92	4	25	103.3	164.89	13.45	659.6	1.16	1.73	3.34
A	1.92	4	25	101.5	165.17	13.21	660.7	1.14	1.7	3.3
V	0.01	0.0	0.0	1.7	2.19	0.21	8.8	0.006	0.06	0.11

When the Tensile/Elongation analysis results of EPDM rubbers prepared in three different combinations were evaluated, it was observed that as the ethylene ratio increased, the tensile strength (Ts/Mpa) increased, but the elongation break force (Eb/%) decreased. Therefore, in the results of the Tensile-elongation analysis, the Ts/MPa value of the Suprene 512 F rubber with the highest ethylene content was observed to be quite high and the Eb/% value to be low. This indicated that the Suprene 512 F sample was mechanically stable. This is probably due to the increase in the number of bonds formed by the carbon atoms in the ethylene molecule and the sulfur used as the vulcanizing agent during the vulcanization of rubber, and is due to the fact that it increases the three-dimensional network formation by forming stable links between the sulfur and the chain segments that can be obtained by chemical reaction.

Rheological Measurements

Rheological measurements were carried out using the machine parameters Time: 3:00 m/s, Torque: 20.93 dN.m, and T: 185 °C. The rheological analysis results according to the parameters are given in Table 6 and Figure 4.

Table 6. Rheological test results of EPDM rubbers prepared at different formulations.

Sample	MH/dN.m	ML/dN.m	Ts1(m:s)	Ts90/(m:s)
Suprene 512 F	11.49	3.77	0.41	1.2
Suprene 512 F (%50) - Dutral TER 4049 (%50)	11.79	3.32	0.4	1.23
Dutral TER 4049	13.32	3.63	0.44	1.37

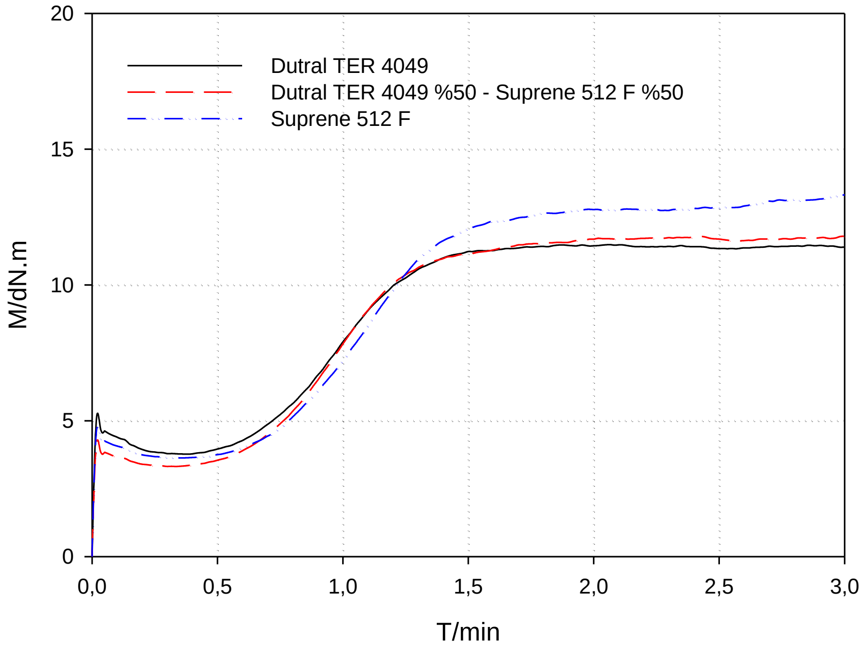

Figure 4. Rheological behaviors of the rubbers.

The results of the rheometer analysis revealed that the maximum cure torque (M/dN.m) of the Suprene 512 F sample was higher than the other two samples; however, 90% of the curing time was later than the other two samples. Comparing the rheological test results of EPDM vulcanizates in three different combinations, it has been observed that the excess of ethylene content plays a diluting role in the rubber and partially dissolves the rubber macromolecule, leading to a decrease in physical entanglement. On the other hand, excess ethylene may have reacted with free radicals produced by thermal degradation, joining the main-net of EPDM rubbers and forming double crosslinking networks. Crosslinking is commonly used to characterize an elastomer or vulcanized rubber, and to indicate three-dimensional network formation by forming stable links between chain segments that can be obtained by chemical reaction with sulfur. This crosslinking is called chemical crosslinking, and is related to the mechanical properties of a rubber net such as crosslink density, tensile strength, and shear modulus or hardness. The tensile strength results of the study also increased with increasing ethylene content, indicating that there may be an increase in chemical crosslink density.

Hardness Analysis

The aging test was performed by keeping the samples in an oven at -10 °C for 48 h. Table 7 shows the hardness test results (i) before aging test at 22 °C, (ii) 48 h aging at -10 °C, and (iii) 6 h after aging test at 22 °C laboratory temperature.

Table 7. Shoremeter results of EPDM rubbers prepared in different formulations.

Sample	**Dutral TER 4049**			**Suprene 512 F (%50)-Dutral TER 4049 (%50)**			**Suprene 512 F**		
Before thermal aging (22°C)	51	51	52	55	55	55	57	57	56
Aging (-10 °C)	55	55	55	65	64	65	69	68	69
6 h after aging	55	56	55	60	60	60	62	62	62

The arithmetic mean of three different samples for each formulation measured in Table 7 is given in Table 8.

Table 8. The arithmetic mean of the shoremeter results.

Sample	**Dutral TER 4049**	**Suprene 512 F (%50)-Dutral TER 4049 (%50)**	**Suprene 512 F**
Before thermal aging (22°C)	51.33	55.00	56.66
Aging (-10 °C)	55.00	64.66	68.66
6 h after aging	55.33	60.00	62.00

In the hardness determination study performed at -10 °C and 24-hour conditioning period, it was observed that the hardness change of Suprene 512 F sample was higher than the others. This is due to the fact that the amount of ethylene in Suprene 512 F is higher than the others, and it causes crystallization in the structure at low temperatures. After conditioning, the hardness of Suprene 512 F, which was left in laboratory conditions at 24°C for 6 h, decreased to 62 SHA.

Conclusions

The increase in the ethylene ratio in the rubber showed a positive change in the mechanical and rheological properties of the produced material. This is probably due to the fact that the excess ethylene ratio increases the number of bonds formed by the sulfur used as the vulcanization agent during the vulcanization of the rubber, and it increases the three-dimensional network formation by forming stable links between the sulfur and the chain segments that can be obtained by chemical reaction. In addition, the increase in the amount of ethylene in EPDM rubber caused crystallization at low temperatures and caused more percent hardness change. This sudden temperature-hardness change causes the rubber products, which are auxiliary materials, to damage the system, shorten their useful life, operate at low efficiency, or fail to meet the standards. Therefore, the reaction of the amount of ethylene to sudden temperature changes should be taken into account while forming the compound formulation. This is due to the fact that the amount of ethylene in Suprene 512 F is higher than the others, and it causes crystallization in the structure at low temperatures. While preparing rubber dough suitable for different demands, the ethylene ratio in the rubber raw material should be noted, considering the effects observed as a result of these experiments.

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Author's Contributions

The contribution of the authors is equal.

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