Development and characterization of Ethylene Propylene Diene Monomer (EPDM) rubber reinforced by green material lignin

Yeşil malzeme lignin ile güçlendirilmiş Etilen Propilen Dien Monomer (EPDM) kauçuğunun geliştirilmesi ve karakterizasyonu

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Abstract

Effects of lignin on the rheological, mechanical, chemical and aging properties of ethylene propylene diene monomer (EPDM) rubber used in the production of sealing profiles were investigated. It is reinforced with carbon black to provide the necessary conditions in all automotive vehicles. However, all automotive manufacturers have started to research biodegradable materials instead of petroleum-based products in vehicles due to environmental problems and human health threats. Therefore, the possibility of using lignin instead of carbon black was investigated. EPDM plate samples were prepared by adding different amounts of commercial lignin, lignin black solution and maleic anhydride modified forms. The effects of lignin as a filler were analyzed rheologically, mechanically and chemically. Also surfaces were checked by scanning electron microscope after ageing. Commercial lignin made EPDM more resistant to ultraviolet and weathering, while unmodified black solution made it less resistant than carbon black. Adding commercial lignin and its modified form instead of carbon black provided the best mechanical properties. Additionally, it was determined that the addition of lignin as a filler did not cause any chemical degradation in the EPDM matrix.

Keywords: Lignin, EPDM, Green materials, Biodegradable fillers

Öz

Sızdırmazlık profilleri üretiminde kullanılan etilen propilen dien monomer (EPDM) kauçuğunun reolojik, mekanik, kimyasal ve yaşlanma özellikleri üzerine ligninin etkileri incelenmiştir. Tüm otomotiv araçlarında gerekli koşulları sağlamak için karbon siyahı ile takviye edilmektedir. Ancak tüm otomotiv üreticileri çevresel sorunlar ve insan sağlığı tehditleri nedeniyle araçlarda petrol bazlı ürünler yerine biyolojik olarak parçalanabilen malzemeler araştırmaya başlamıştır. Bu nedenle karbon siyahı yerine lignin kullanma olasılığı araştırılmıştır. Ticari lignin, ligninin siyah çözeltisi ve maleik anhidrit ile modifiye edilmiş formlarının farklı miktarlarda eklenmesiyle EPDM plaka numuneleri hazırlanmıştır. Ligninin dolgu maddesi olarak etkileri reolojik, mekanik ve kimyasal olarak analiz edilmiştir. Ayrıca yaşlandırıldıktan sonra yüzeyler taramalı elektron mikroskobu ile kontrol edilmiştir. Ticari lignin, EPDM'yi ultraviyole ve hava koşullarına karşı daha dirençli hale getirirken, modifikasyonsuz siyah çözelti, onu karbon siyahından daha az dirençli hale getirmiştir. Karbon siyahı yerine ticari ligninin ve modifiye edilmiş formunun eklenmesi en iyi mekanik özellikleri sağlamıştır. Ayrıca dolgu maddesi olarak lignin ilavesinin EPDM matrisinde herhangi bir kimyasal bozunmaya neden olmadığı belirlenmiştir.

Anahtar Kelimeler: Lignin, EPDM, Yeşil malzemeler, Bozunabilir dolgu malzemeleri

1 Introduction

EPDM is a synthetic rubber which is produced by unsaturated diene monomer addition during the copolymerization of ethylene and propylene. Ethylene propylene diene monomer rubber is widely used in sealing profiles, roofing materials, sporting goods, gaskets, barriers, hoses, cables, etc. due to its ultraviolet resistance, waterproof structure, ability to form mixtures at low cost, oil retention properties, ozone and heat resistance, and good mechanical/physical properties [1-3]. However, reinforcing fillers such as organic or inorganic materials are always required in the EPDM matrix to improve its physical, chemical, rheological, morphological, and aging properties [4]. Inorganic fillers such as carbon black (CB) and white fillers (talk, silica) are harmful for health and the environment. Organic biodegradable fillers such as lignin and cellulose started to be researched recently in many industries because of limited usage of inorganic fillers [4-6].

Lignin, a three-dimensional biopolymer, is the second most abundant renewable, natural, and degradable resource, next to cellulose [7,8]. It is a macromolecule composed of 9-carbon phenol propane units (p-coumaryl alcohol, coniferyl alcohol, sinapyl alcohol) linked together by different types of bonds. Its chemical functional groups include hydroxyl, methoxyl, carbonyl, and carboxyl groups, which confer benefits and special functional properties to lignin, such as reinforcement, stabilization [9], ultraviolet absorption, biodegradability, and antifungal and antibiotic activity [10-12].

Many studies [13-16] and patents [17-21] show that lignin can be used in rubber formulations as filler instead of carbon black due to its good physical, mechanical and chemical properties such as low density, non-toxic property, recyclability and non-conductive property. Obtaining value-added products from lignin such as usage of it as filler, is important in terms of environmental and economic factors. In order to be used as a reinforcement in rubber, the particle size of the lignin and the strong interfacial bond with the rubber matrix should be adjusted. In previous studies, lignin was used instead of resorcinol in the hexamethylenetetramine, resorcinol and hydrated silica (HRH) bonding system for ethylene propylene diene monomer (EPDM)/microcrystalline cellulose (MCC) composites [22,23]. There are not many studies in the literature where lignin is used as reinforcement in EPDM rubber. Microcrystalline cellulose (MCC) and lignin were used instead of EPDM and carbon black and their effects were investigated together [24,25]. However, in these studies, lignin were used in ready-to-use powder form. The aim of this study is to investigate the distribution of lignin black solution obtained by precipitating from pulp black liquor in our pulp production facility with Indulin AT, a new pine kraft lignin commercialized by Meadwestvaco for the last 60 years [26], in the EPDM matrix and its effect on EPDM. Thus, our main goal is to investigate the usability of lignin as a biodegradable filler material instead of petroleum-based fillers in the rubber industry.

2 Material and method

2.1 Material

The EPDM was supplied by the company Standard Profile (Duzce, Turkey). The production formulation of EPDM is given in Table 1. The additives were given with units of parts per hundred parts of rubber (phr). In the components used in the formulas, the amounts of EPDM (100 phr), oils (63 phr), initiator (11 phr), white fillers (75 phr) such as calcium carbonate ($CaCO_3$) and silicon dioxide (SiO_2) and sulphur (6.5 phr) were constant, while the amounts of CB and lignin were changed. Commercial lignin formulas are named as CL, those prepared by black solution are named as BS, while the forms of both lignins modified with maleic anhydride are named as CL-MA and BS-MA.

Table 1. The production formulation of EPDM plates

Sample	CB	Lignin
CG	165	0
CL5	160	5
CL10	155	10
CL-MA5	160	5
CL-MA10	155	10
BS5	160	5
BS10	155	10
BS-MA5	160	5
BS-MA10	155	10

Lignin, commercial name Indulin AT, was supplied by Vestwaco (Virginia, USA), and lignin in the form of black solution was obtained from hazelnut shell waste in the pulp pilot-scale production facility established within the Düzce University Agricultural Waste Industrial Recycling Application and Research Center. The concentration of commercial lignin (Indulin AT) was 235.89 g/L 60 wt% ethanol solution at a solid-liquid ratio of 300 g lignin/L solvent. The number-average (M_n) and mass-average (M_w) molar mass values were $M_n = 1336$ and $M_w = 4721$, while the polydispersity value was 3.54. The phenolic hydroxyl group content for commercial lignin was 2.07 mmol/g [27].

2.2 Green composites manufacturing

Nine different compounds were prepared by adding 5.0 phr of commercial lignin (CL5), 10.0 phr of commercial lignin (CL10), 5.0 phr of commercial lignin modified with maleic anhydride (CL-MA5), 10.0 phr of commercial lignin modified with maleic anhydride (CL-MA10), 5.0 phr of black solution (BS5), 10.0 phr of black solution (BS10), 5.0 phr of black solution modified with maleic anhydride (BS-MA5), and 10.0 phr of black solution modified with maleic anhydride (BS-MA10). A total of 40 different plates were prepared, five for each compound, and 5 of the currently used EPDM paste were prepared as a control group (CG) for comparison. Thus, the analyses were performed on 45 different plates.

The raw materials of EPDM were firstly stirred in a lab-scale mixer with a capacity of 1.5 L (Carter Bros, F270, Manchester, England). Temperature was changing between 23 °C ± 2 °C to 100 °C. The duration of stirring was 5 min while the speed was 47 rpm. The compounds were passed through a lab-scale cylinder (ESER, Ankara, Turkey). After the cylinder the compounds were pressed for 7.5 min at 180 °C with a lab-scale compression press (ESER, Ankara, Turkey). Thus, EPDM plates were prepared for mechanical, chemical, and aging analysis.

2.3 Characterization of green composites

2.3.1 Fourier-transform infrared (FTIR) spectroscopy analysis

FTIR spectroscopy is a powerful tool for monitoring vibrational energy levels in regions of different molecules. Changes in chemical properties are often monitored by FTIR spectroscopy, which is a very sensitive and non-destructive technique. It was performed using Shimadzu IRPrestige 21 spectrometer. FTIR spectra were recorded in the range of 450–4000 cm^{-1} at room temperature.

2.3.2 Mechanical properties

The mechanical analysis of the EPDM plates were performed in tensile, tear, and elongation tests. The tensile and elongation tests were performed according to DIN 53504 (2017), and the tear tests were performed according to DIN ISO 34-1 (2015) at 23 °C. The tests were performed via Zwick testing machine (Zwick Roell Z010, Ulm, Germany) which is a computer-controlled and has a speed of 200 mm/min. Six samples were used for testing.

2.3.3 Rheological properties

EPDM plates were analysed rheologically in terms of viscosity, scorch, and moving die rheometer (MDR). The Mooney viscosity tests were applied to see the simulation of flowing of the rubber in extruder. The duration of the test is (1+4) min at 100 °C. The aim of the scorch test is to reveal behavior of rubber during the period it remains in the extruder. The duration of the test is (1+20) min at 121 °C. The MDR tests were alse performed in order to measure the vulcanization times of ts2 (scorch time) and t90 (the 90% optimum vulcanization time of rubber) for 2.5 min at 180 °C. All of the rheological analysis were performed according to the standard ASTM 1646 (2018) with the machine of ALPHA Technologies MDR 2000 (Ohio, USA).

2.3.4 Deformation properties as permanent set

In rubber industry, deformation properties were measured as the term of permanent set test. The samples were firstly aged for 22h + 2h at 100 °C. After thermal aging the heights of the samples were measured with a device (Absolute 570, Mitutoyo, Aurora, USA) in order to calcuate the deformation according to the following equation:

$$Permanent\ set\ (\%) = \frac{h_i - h_f}{h_i - h_0} x100 \qquad (1)$$

The sample height before thermal aging is h_i, the sample height after thermal aging is h_f and the compression distance is h_0. Six samples were tested according to the standard DBL 5571 (2011).

2.3.5 Artificial weathering test

Natural weathering analysis take a very long time and have difficulties in reproducibility. For this reason, artificial weathering test with natural weathering conditions such as ultraviolet (UV) radiation, temperature, humidity and irradiance was applied to EPDM samples. The artificial weathering test was performed for 250 h in a weathering machine (Atlas Ci4000, Illinois, USA) according to Fiat Automotive Standard SAE J 2527 (2004). The UV radiation was between the wavelength of 300 nm to 400 nm at 70 °C. The relative humidity of analysis was 50% and irradiance intensity was 0.55-W/m².

2.3.6 Scanning electron microscopy (SEM) analysis

The SEM analysis were performed to the surfaces of the EPDM samples in order to characterize them morphologically by a machine (FEG 250, Oregon, USA). Since the plate surfaces were non-conductive, they were gold-plated before being placed in the device to make them conductive. After scanning electron micrographs were taken, EDX spectra were analysed for the chemical contents.

3 Results and discussions

3.1 Fourier-transform infrared (FTIR) spectroscopy analysis

The chemical compositions of the EPDM plates were investigated by FTIR spectroscopy, and the results are shown in Figure 1.

Rubbers have complex spectra due to overlapping asymmetric, symmetric, and bending vibrations. The main chain in EPDM interacts at 2925 cm⁻¹, 2853 cm⁻¹ which are asymmetric and symmetric stretchings. It contains also C-H bending vibrations at 1460 cm⁻¹, 1377 cm⁻¹ that occurs due to CH_2 and CH_3 respectively in the ethylene, propylene, and diene monomers of the EPDM structure.

The spectra of the CS_2 group revealed crosslinking carbon-sulfur interactions, as shown at approximately 2320 cm⁻¹ and approximately 2180 cm⁻¹.

The spectra of the CG, CL5, CL10, CL-MA5, CL-MA10, BS5, BS10, BS-MA5 and BS-MA10 were the same. It means that lignin did not degrade the matrix structure.
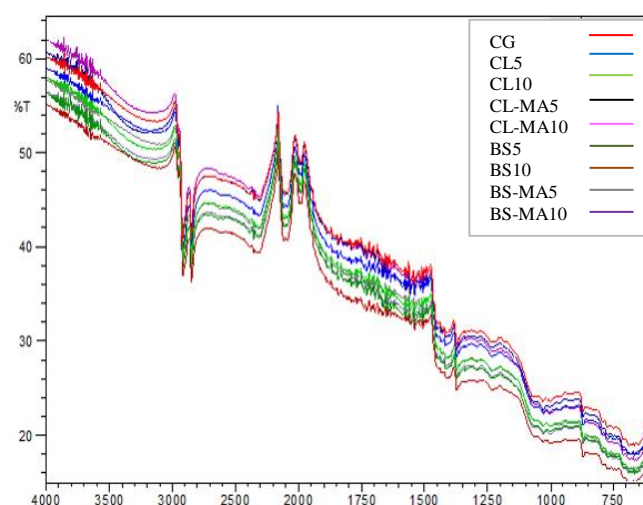

Figure 1. FTIR spectra of EPDM plates

3.2 Mechanical properties

The mechanical values such as tensile strength, tear strength and elongation at break of lignin filled EPDM samples are shown in Figure 2, Figure 3 and Figure 4, respectively.
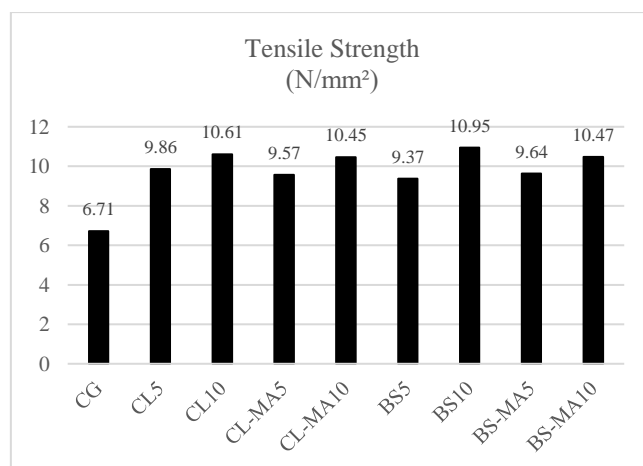

Figure 2. Tensile strength values of lignin filled EPDM

As shown in Figure 2, adding lignin to the currently used EPDM rubber increases tensile strength values, regardless of the lignin type and ratio. Xu et al. obtained similar results

after adding the lignin to the EPDM matrices [28]. This is attributed to the presence of a less cross-linked lignin phase, which makes stress transmission through the EPDM matrix difficult due to poor interface incompatibility [29]. Lignin modified with maleic anhydride further increases tensile strength values. This increase is probably due to the fact that after modification, lignin provides an increased contact surface with the EPDM, which promotes a better stress transfer [30,31].
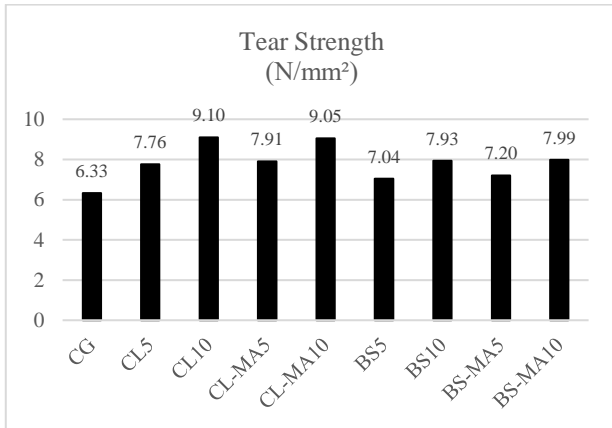

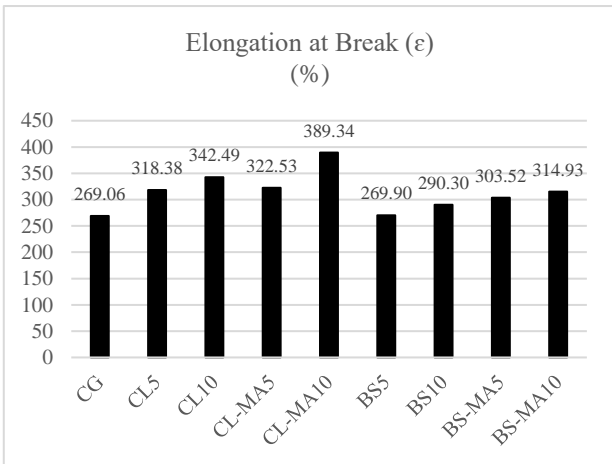**Figure 3.** Tear strength values of lignin filled EPDM

Figure 4. Elongation at break values values of lignin filled EPDM

Figure 3 shows that lignin increased the tear strength of the EPDM rubber with similar trend as tensile strength. Commercial lignin had more effect on the tear strength than did the black solution. The increase in the elongation at break values can be attributed to the 3D aromatic structure of lignin, which allows for high modulus. In addition, this 3D aromatic structure provided rigidity and more interaction between lignin and EPDM molecular segments [32]. As shown in Figure 4, lignin increased the elongation at break values. Commercial lignin had more effect on elongation than the black solution. The highest elongation values were those for maleic-anhydride-modified lignin. Thus, the modification of lignin with maleic anhydride increased the elongation of the EPDM rubber. This result means that

adding lignin makes the rubber more elastic and more resistant, as desired.

3.3 Rheological properties

The rheological values such as mooney viscosity, mooney scorch, and vulcanization times as ts_2 and t_{90} of lignin filled EPDM samples are shown in Figures 5 to 7, respectively.
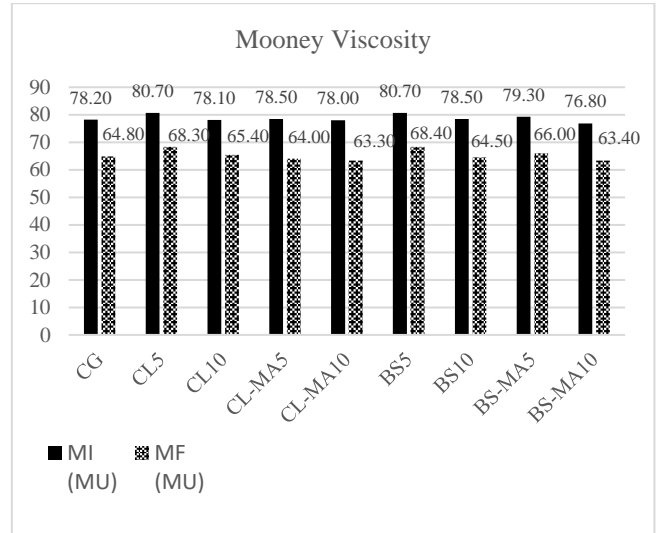

Figure 5. Mooney viscosity values of lignin filled EPDM

The initial viscosity value which is known as MI and the final viscosity value known as MF are given in Figure 5. Adding lignin caused an insignificant increase in the viscosity, except for CL-MA10 and BS5.
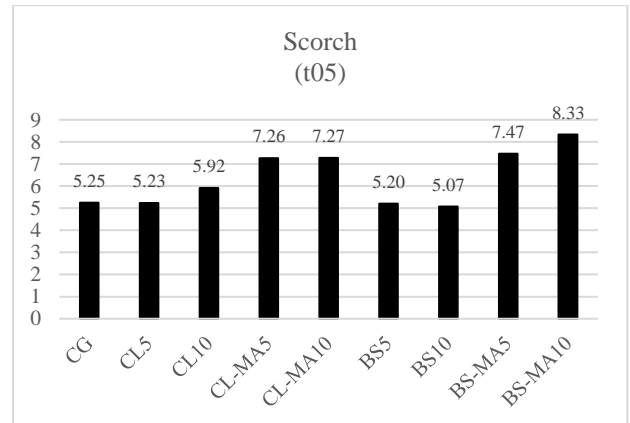

Figure 6. Mooney scorch values of lignin filled EPDM

As shown in Figure 6, lignin addition had no significant effect on the Mooney scorch of EPDM rubber. However, preparing the plates with the maleic-anhydride-modified lignin increased the scorch values. This can be attributed to the reduced molecular motion of modified lignin and the presence of stronger EPDM-lignin interaction. Therefore, the torque values required for the vulcanization process will decrease and lower forces will be needed to rotate the rotor [33].

Figure 7 shows that adding lignin did not cause a change on vulcanization times known as ts_2 and t_{90}. An increase is seen in vulcanization times in modified black solution lignin. This can be attributed to the fact that the modified lignin acts as an activating agent to reduce the burning time and to reduce adhesion and chain mobility in the matrices. This also means a faster heat transfer due to the homogeneous lignin distribution [25]. However, rheological results show that any change in process conditions necessary during the production of EPDM rubber with lignin filling.
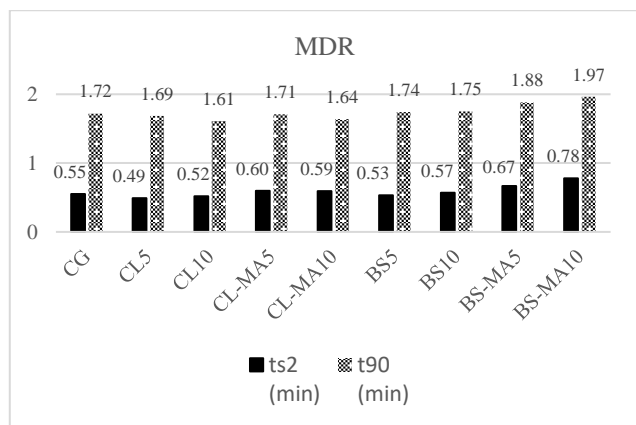

Figure 7. Vulcanization times of lignin filled EPDM

3.4 Deformation properties

Permanent set values of the deformation properties are important in the rubber industry. Permanent set values for the rubber are shown in Figure 8. Adding lignin caused a small increase in permanent deformation values. Therefore, overall, it can be said that lignin has influenced positively on the permanent set values.
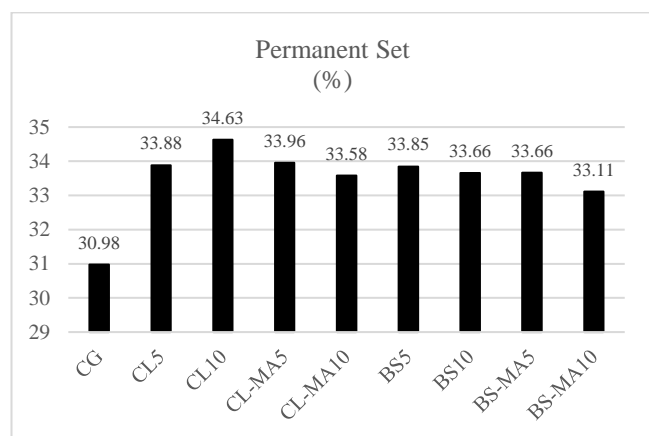

Figure 8. Permanent set values of lignin filled EPDM

3.5 Artificial weathering test

The lignin filled EPDM samples were climated for 250 h in the artificial weathering machine and were controlled visually after aging. As shown in Table 2, there are no stains, no cracks, or no color changes on the surfaces of samples prepared by adding commercial lignin, while there are color changes on the surfaces of EPDM plates without lignin. It can be said that commercial lignin with or without

modification increased ultraviolet or weathering resistance of the EPDM plates. In contrast, the black solution made the surfaces worse and caused staining on the surfaces of the EPDM plates. However, if the black solution was modified with maleic anhydride, it increased the resistance of the EPDM rubber against ultraviolet and weathering.

Table 2. Visually controls after 250h weathering

EPDM Plate	250 h of Kalahari Aging
CG	
CL5	
CL10	
CL-MA5	
CL-MA10	
BS5	
BS10	
BS-MA5	
BS-MA10	

3.6 SEM analysis

The SEM pictures taken of the EPDM plates prepared by the addition of lignin are shown in Figure 9. Lignin fillers except for modified black solution were homogeneously dispersed in the EPDM rubber, and no considerable difference is observed with increasing amounts of it. The white particles seen on the surfaces of the EPDM plates shown in Figure 9a to 9d were white fillers such as $CaCO_3$ and SiO_2, which were added in amounts of 25 phr and 20 phr, respectively. Agglomeration, cracking, individual fibrils, and voids were not seen in the SEM photos. This result means that lignin did not chemically degrade in the EPDM matrix. However, as shown in the surface of the EPDM plate in Figure 9e, black solution lignin modified by maleic anhydride caused chemical degradation in the EPDM matrix. The SEM photo of it has been enlarged 2 times to aid in interpreting what happened. Maleic anhydride migrated to the surface after ultraviolet irradiation because of high impurity.

The samples were burned to collect the ash which was analyzed with EDX. Major components of the ash were oxygen (O), sulfur (S), calcium (Ca), and zinc (Zn) as seen in Table 3. The atomic percents of sulfur, calcium, and zinc were very similar for each plate samples. The observed calcium indicates that the EPDM article was reinforced with calcium carbonate ($CaCO_3$) as well as carbon black. The observation of sulfur and zinc means that the EPDM article had a sulfur cure system. Sulfur came from the curatives such as cure accelerators and sulfur, while zinc came from zinc oxide. Zinc oxide was used as a cure activator along with fatty acids such as stearic acid in sulfur-cured rubber composites.

Table 3. Atomic percents of EPDM samples.

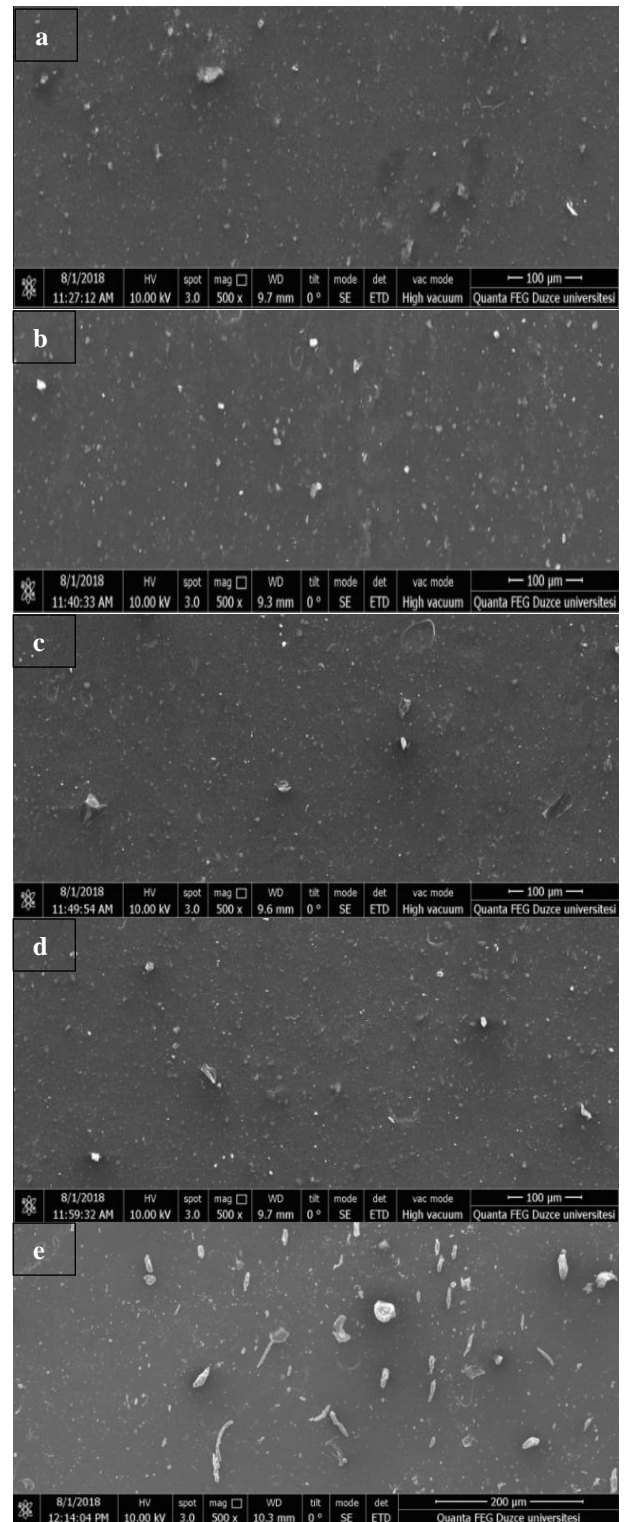| EPDM Plate	Karbon (C)	Oksijen (O)	Silisyum (Si)	Kükürt (S)	Kalsiyum (Ca)	Çinko (Zn)
1	83.63	5.24	3.14	1.53	4.7	1.76
2	84.14	5.38	3.18	1.46	4.58	1.26
3	84.39	5.2	2.94	1.33	4.5	1.63
4	86.03	4.44	2.52	1.31	3.94	1.76
5	83.59	5.38	3.21	1.5	4.81	1.51
6	83.9	5.29	2.98	1.28	4.77	1.78
7	84	5.27	2.98	1.52	4.56	1.67
8	83.08	5.5	2.96	1.61	4.63	2.22
9	82.03	7.19	2.93	1.56	4.36	1.92

Figure 9. SEM images of (a) EPDM plate, (b) EPDM-L2 plate, (c) EPDM-L4 plate, (d) EPDM-L6 plate, and (e) EPDM-L8 plate

4 Conclusions

Lignin was investigated in detailed as a filler instead of carbon black for EPDM rubber. The lignin made the EPDM more elastic and more resistant by increasing the tear strength and elongation at break values. The commercial lignin type and modification of lignin with maleic anhydride were more effective at enhancing the mechanical properties of the EPDM. After adding the lignin to EPDM rubber, it could be vulcanized with the same process conditions. However, modification of lignin caused slower production, according to the rheological results. Commercial lignin made the EPDM more resistant to ultraviolet and weathering conditions, while the black solution without modification made it less resistant than that of carbon black. Lignin, except for the modified black solution, does not chemically degrade in the EPDM matrix. While lignin improves the mechanical properties of EPDM rubber compounds compared to carbon black, it does not cause any change in process conditions. This result means that lignin can be used as a filler in EPDM rubber instead of carbon black. Thus, petroleum-based materials can be replaced by biodegradable materials with further studies.

Acknowledgements

Conflict of Interest

The author declare that they have no conflict of interest.

Similarity Rate (iThenticate): 19 %

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