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The effect of Cumin Black (*Nigella Sativa L.*) as bio-based filler on chemical, rheological and mechanical properties of epdm composites

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Abstract

One of the significant problems of our time and future is environmental pollution. There are many factors that cause environmental pollution and the main concerns are waste material. Since production, consumption and service activities have increased with rapid industrialization and increasing population. Waste assessment is a process that includes minimization, separate collection at source, intermediate storage, pre-treatment, the establishment of waste transfer centers, recovery and disposal when necessary, which are qualified as outputs as a result of activities such as production, application and consumption. The purpose of waste assessment is to ensure the process of wastes generated by human action without harming the environment and human health. In this context, re-evaluation of agricultural and aquaculture products that turn into waste after being used as a product is important both in terms of economic and environmental pollution. Herein, the use of cumin black pulp, which is waste at the end of black seed oil production, as a bio-based filler material in ethylene-propylene diene rubber (EPDM) was examined. Accordingly, the effects of cumin black pulp added to the EPDM matrix at different content on the rheological, mechanical and crosslinking degree of EPDM were determined. With the use of 10 phr cumin black pulp, the mechanical and rheological properties of EPDM and the degree of crosslinking increased. The tensile strength and elongation at break of the EPDM/CB composites increased up to 11 MPa and 480% with the addition of 10 phr CB, respectively. In addition, it was revealed that the vulcanization parameters were also enhanced. Consequently, it has been concluded as a result of the analysis that the waste cumin black pulp can be used as a filling material in the EPDM matrix. Thus, it has been seen that a product in the state of waste can be recovered and become an economic value.

1. Introduction

Rubber is a significant material with a multi-purpose and wide range of uses and it is a polymeric material obtained naturally from the tree sap of some plants or artificially produced from petroleum and alcohol [1]. Rubbers are widely used in many industrial applications [2]. For example, rubber is the main component of the low-pressure hoses of the wheels and the car body connections in the automotive industry. In addition, fuel and brake hoses, windshield wipers, transmission belts, gaskets, axle bellows, radiator and air hoses, door and window profiles, oscillation and vibration wedges, and insulation elements are other examples of rubber materials used in the automotive industry [3–5].

Rubbers differ from other polymeric materials due to their unique characteristics. In the unstressed state, rubbers are amorphous and elastic over glass transition temperatures, conversely, plastics are crystalline and are used under glass transition temperatures to maintain their stability [6]. Rubbers gain a significant elasticity at room temperature due to the elongation properties of the molecular chains that are in the form of a ball [7]. Under the influence of high temperature and deforming forces, they show viscous flow and can be shaped under suitable conditions. In addition, with increasing temperature, the fluidity of the material increases and they exhibit a thermoplastic behavior [8,9].

The use of rubber in daily life increased with Charles Goodyear's discovery of vulcanization in 1843. Goodyear and Hancock added sulfur to the rubber to eliminate the difficulties in use such as softening of the rubber in the heat and embrittlement in the cold medium, and heated

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rubber up to 130-140°C after shaping, and this process is called vulcanization [10,11].

Terpolymer EPDM, which is one of the synthetic rubber types, is synthesized by the polymerization reaction of diene together with ethylene and propylene. With the participation of diene in the reaction, a double bond, that is, unsaturation occurs in the chain [12]. This chemical modification allows curing with sulfur as well as peroxides and mixing with other polymers [13]. Since the unsaturation is in the side group in EPDM, the olefinic segments are saturated [13]. Therefore, EPDM-based products are rubbers with very high resistance to oxygen, ozone and chemicals [14]. Since EPDM is nonpolar, it is resistant to polar chemicals. While EPDM is resistant to acids and bases, it is not resistant to oils and is highly affected by aromatic, aliphatic and chlorinated hydrocarbons [15].

Depending on the physical properties desired in the field of use as a final product, there are various additives and fillers with different properties in the composition of rubber-based materials, as well as some natural or synthetic polymers, and these substances are added to the unvulcanized mixture in a certain amount in the rubber dough preparation process [16]. Fillers are added to the composition to improve the physical properties of the product, give a specific functionality to the product, or reduce the unit cost [17]. One of the most commonly used filling materials in the rubber industry is carbon black and it improves mechanical properties of rubbers. In addition, the use of carbon black causes an increase in hardness, breaking strength and electrical conductivity and a decrease in elastic modulus after vulcanization in rubbers [18].

Despite all these advantages it provides to rubber materials, it has been determined that carbon black is a genotoxic material, and its use as a filling material is very harmful for both employees and the environment [19,20]. For this reason, in recent years, the use of bio-based filling materials has been emphasized in the rubber industry instead of filling materials such as carbon black, which are known to be harmful, considering both the sustainable environment and employee health. For this purpose, natural components such as walnut shell, fish scale, peanut shell, which are in the form of waste, can be used as filling material [21]. Thus, both a waste material is evaluated and the negative effects caused by carbon black can be minimized.

Cumin black (*Nigella sativa L.*), a flowering plant, mostly grows in Asia, the Middle East and the Mediterranean. Cumin black, which has a peppery flavor, is used as a spice in Indian and Middle Eastern. It is consumed in powder form or oil is obtained by squeezing the seeds [22,23]. Today, cumin black is a valuable product used in spice, functional food, herbal drug preparations, health and cosmetics sectors [24]. Turkey is one of the leading countries in black seed production due to its suitable climate and land conditions. The composition of the seed contains 30-45% fixed oil, 0.01-0.5% essential oil, 20-30% protein, alkaloid bitter substances and saponins [25]. Due to its high oil content, black seed oil production has been increasing in recent years. After the black seed oil is obtained, the remaining pulp is generally used as animal feed [25].

In this study, the use of cumin black pulp, which is waste after black seed oil production, in EPDM rubber was examined. To the best our knowledge, the use of cumin black pulp, which is waste as a result of cumin black oil production, as a biodegradable filling material in EPDM has not been found in the literature. In this direction, cumin black pulp was added to the EPDM matrix in different amounts and its effect on the rheological, mechanical and chemical properties of the final product was examined.

2. Method

The cumin black pulp (CB) was obtained from a local cumin black seed oil producer. Before the use of CB, a filler material, it applied some pre-treatment. In this regard, cumin black pulp is washed with de-ionized water to remove the impurities. The cleaned CB was dried in an oven at 50 °C. The dried CB was milled and then sieved with different mesh-sized sieves. CB particles below 250 micrometers were used throughout the study. In the second step, the unvulcanized EPDM compound and CB were mixed with a Kneader-type closed mixer until a homogeneous dough is obtained at 60 °C. After that, the obtained compound was compressed in a two-roll mill [14].

Table 1. The recipe applied for the synthesis of EPDM and EPDM/CB composite materials

Materials	Function	Amount (phr)
KELTAN 9650Q	Rubber	100
Carbon Black	Filler	1
Zinc Oxide	Activator	1.5
Mineral Oil	Lubricant	32
Stearic Acid	Activator	1
TAC/50	Coagent	1
Perkadox	Crosslinker	5
Cumin Black pulp (CB) (0CB-5CB-10CB-15CB)	Biobased Filler	0-5-10-15

In characterization studies, the effects of CB added to the EPDM matrix as a bio-based filling material at different rates on the rheological, mechanical and chemical properties of the material were investigated.

The rheological properties and vulcanization parameters of EPDM and EPDM/CB composite materials were determined with a moving die rheometer (MDR) device. A universal mechanical testing machine (Shimadzu AGS-X) was used to determine the mechanical properties. 2mm EPDM samples were cut into dog bone shapes by ASTM D412 standard and all mechanical analyzes were performed in accordance with ASTM D412 standard.

The crosslinking density of EPDM and EPDM/CB composites was determined by the Soxhlet extraction method. The crosslinking density of the prepared composites was calculated via Equation 1, where w_i is the initial weight of the composite and w_f is the final weight of the composite. Hexane was used as solvent throughout the experiment and the extraction process were carried out at 75 °C.

$$Gel\ Content, \% = w_f / w_i * 100 \quad (1)$$

The crosslinking degree was also calculated by swelling test. The EPDM and EPDM/CB composites were prepared 1cm x 1cm with a thickness of 2 mm and the toluene was utilized. The swelling ratio was determined by Equation 2.

$$Swelling\ Ratio, \% = (w_f - w_i)/w_i * 100 \quad (2)$$

3. Results and Discussion

In this study, the use of cumin black pulp, which is waste after cumin black seed oil production, a filling material in EPDM rubber was investigated. Accordingly, different amounts of CB particles as bio-based filling materials were added to the EPDM matrix and the effects of the amount of CB on the rheological, mechanical and chemical properties of the composite material were investigated.

3.1. Rheological properties

Vulcanization is the process of crosslinking long rubber chains to form a three-dimensional elastic structure. The vulcanization process can usually occur with the help of sulfur or sometimes with a different chemical such as peroxide. Vulcanization is a chemical process that improves the physical properties of elastomer mixtures. On the other hand, rheology is the science of the flow and deformation of matter. Shear stress deals with the relationships between shear deformation and time. It covers the study of the mechanical properties of gases, liquids and solids. Therefore, characterization of rheological properties and vulcanization parameters has important in the evaluation of rubber materials [26,27].

Torque curves of EPDM and EPDM/CB composite materials produced are shown in Figure 1. As seen in Figure 1, the torque values of the material increase up to 10 phr CB content. However, a significant decrease is observed in the torque value of the synthesized composite material when the amount of CB used is above 10 phr. Increasing the amount of CB may cause a decrease in the homogeneity of the rubber mixture, which can lead to the formation of void regions (fail points) in the rubber matrix. These fail points may cause the torque values of CB15 to decrease under the applied stress actuation.

In Table 2, the vulcanization parameters of the synthesized EPDM and EPDM/CB composite materials are tabulated. The effect of CB added into the EPDM matrix on t_{s2}, t_{90} and M_H-M_L values was investigated in the evaluation of vulcanization parameters.

Table 2. Vulcanization parameters of EPDM and EPDM/CB composite materials

Samples	t_{s2} (sec)	t_{90} (sec)	M_H-M_L (N.m)
0CB	38.92	95.86	11.85
5CB	40.12	93.87	12.17
10CB	43.81	90.24	13.41
15CB	34.53	101.63	11.26

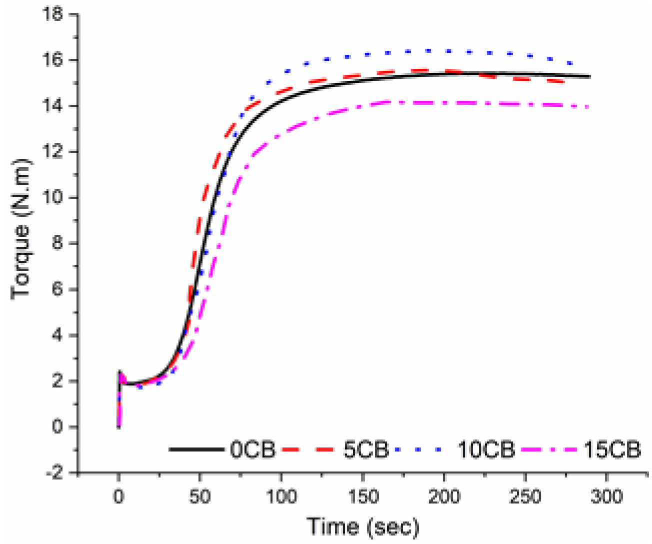

Figure 1. Torque curves of EPDM and EPDM/CB composite materials

The M_L and M_H values represent the minimum and maximum torque, respectively. M_L value is the smallest torque value at which vulcanization starts and is related to mixing conditions. The M_H value is related to properties such as tensile, tear and rupture strength. t_{s2} time is the scorch time of the rubber mixture. Scorch time refers to the time to start vulcanization. The short scorch time causes the rubber to cure prematurely. When there is an early curing problem, shape stability and workability decrease and the mechanical properties of rubber decrease. Therefore, it is desirable for the t_{s2} value should be long. The t_{90} value is the time it takes for 90% of the EPDM to cure. 90% is the optimum curing time. If the vulcanization process is completed before reaching the t_{90} time, deformation of the rubber and a decrease in mechanical properties may occur.

When the effect of CB on t_{s2} is examined, it is seen that CB added up to 10 phr increases the flux time of the rubber. The t_{s2} time of the material is significantly reduced when the amount of CB used is above 10 phr. At t_{90} values, a similar trend is observed for t_{s2} time. In addition, the optimum curing time of the rubber decreases until the use of 10 phr CB. With the increasing amount of filler material, an increase in the optimum curing time is also observed. Furthermore, when the torque difference values (M_H-M_L) related to the crosslinking degree of rubber materials were examined, the highest torque difference value was obtained in the CB10 sample. Considering the vulcanization parameters, it is concluded that the addition of CB until 10 phr positively affects the vulcanization parameters of the material. Thus, it has been understood that waste CB particles can be used as a bio-based filler in the EPDM rubber.

3.2. Tensile properties

In the preparation of rubber materials, the production of high mechanical properties for the area to be used is one of the most important parameters. Therefore, the characterization of the mechanical properties of rubber materials is significant for the evaluation of the rubber material. In this study, the effects of bio-based CB particles used as filler material on the mechanical properties of EPDM were investigated and the analysis results were given in Figure 2-4. Tensile strength, elongation at break, hardness and toughness (energy) properties of EPDM and EPDM/CB composites were taken into account in the evaluation of mechanical properties.

In Figure 2, the effects of CB on the tensile strength and elongation at break values of the prepared samples are given. Tensile strength is the maximum amount of load the polymer can tolerate without breaking when two forces applied to the polymer in the same way but in opposite directions. When the applied force overcome the tensile strength of the polymeric material, rupture happens in the polymeric material [28]. When the tensile strengths of EPDM and EPDM/CB samples were examined, it was observed that the tensile strength of the material increased up to CB10 sample, while the CB0 and CB5 samples gave similar results. In parallel with the increase in the amount of CB used, the tensile strength also decreased. On the other hand, elongation at break is the rate of elongation of the material at full break during the tensile test applied to the material. The elongation value is usually expressed as a percentage, so it is not a value dependent on the unit area over which the force is applied. As can be seen from Figure 2, CB used as filler material increased the elongation at break of the material and an elongation value of approximately 500% (CB10) was reached. The results of elongation at break and tensile strength results are similar to each other, and it is revealed that the mechanical properties increase with the use of 10 phr CB in both analyzes.

The effects of CB on the toughness and hardness of the prepared composites are given in Figure 3 and Figure 4, respectively. Toughness refers to the total energy absorbed by the material until it deforms. Toughness is an engineering property that matters when it comes to a material's ability to withstand an impact without breaking. The toughness of a material is equal to the area under the stress-strain graph of the material [29]. As can be seen in Figure 3, it is seen that CB used as a bi-based filling material increases the toughness values of EPDM by up to 10 phr CB content. Therefore, it has been concluded that CB added to the EPDM matrix increases the ductility of the produced composite materials. With the addition of more than 10 phr of CB to the EPDM matrix, the ductility of the EPDM composite decreased and it became a more brittle material.

Hardness is the resistance of a material against a hard object immersed in its surface, and it is of great importance as the hardness values are directly related to the strength of the materials [30]. Figure 4 shows the effect of the amount of CB used as a bio-based filler on the hardness of EPDM composites. Compared to Neat EPDM (0CB), EPDM with different CB content had a reduction in hardness values. In parallel with the increase in the amount of CB added to the EPDM matrix, the hardness values also decreased, that is, the material is in a softer form and therefore its resistance to the applied force decreases.

When the mechanical analysis results were evaluated, it was concluded that the tensile properties of the material increased in the use of CB, which is used as a filling material, up to 10 phr. On the other hand, the use of CB above 10 phr decreased the mechanical properties., It is understood that the optimum amount of CB is 10 phr considering the mechanical analysis results. In addition, the results of the mechanical and rheological analysis are compatible with each other. It is also understood that CB can be used in the EPDM matrix as a bio-based filler material.

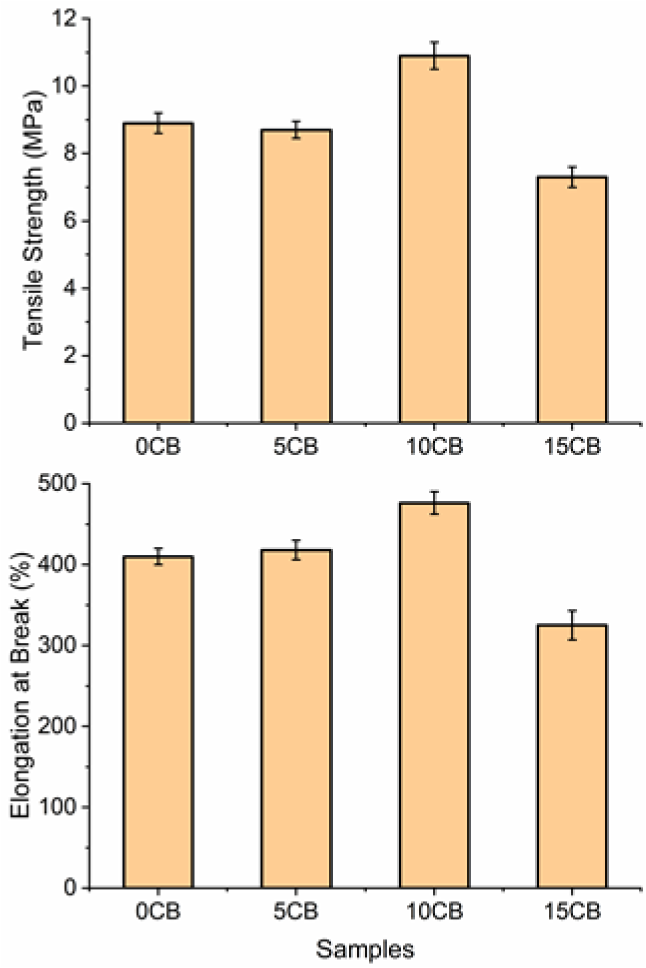

Figure 2. Tensile strength and elongation at break values of EPDM and EPDM/CB composite materials

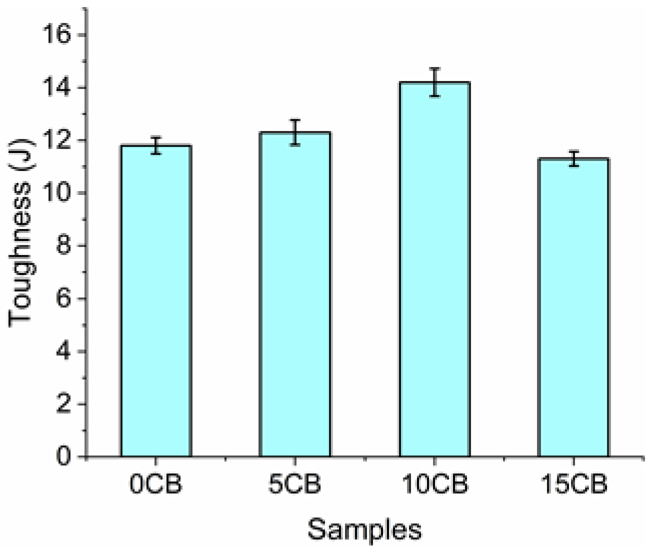

Figure 3. Toughness values of EPDM and EPDM/CB composite materials

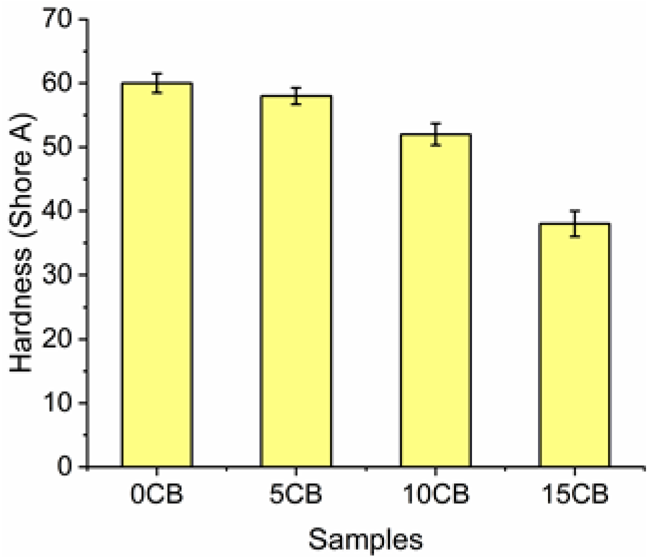

Figure 4. Hardness values of EPDM and EPDM/CB composite materials

3.3. Gel content and swellling ratio of EPDM composites

The gel content (crosslinking density) of rubber materials is directly related to their mechanical properties and is therefore an important analysis method for the evaluation of the material. In general, the traditional Soxhlet extraction method and swelling ratio analysis are frequently used to the determine the gel content of rubber materials [30].

Figure 5 shows the effect of the amount of CB used as a bio-based filler on the gel content of EPDM composites. Gel content was calculated using Equation 1. Accordingly, the mass change during the extraction process was taken into account. The high gel content of the rubber material indicates that the mass loss will be less. As can be seen in Figure 5, the gel content of the material increased with the addition of up to 10 phr of CB and the highest gel content was reached in the CB10 sample at about 86.5%. With the increasing amount of CB, the gel content decreased significantly.

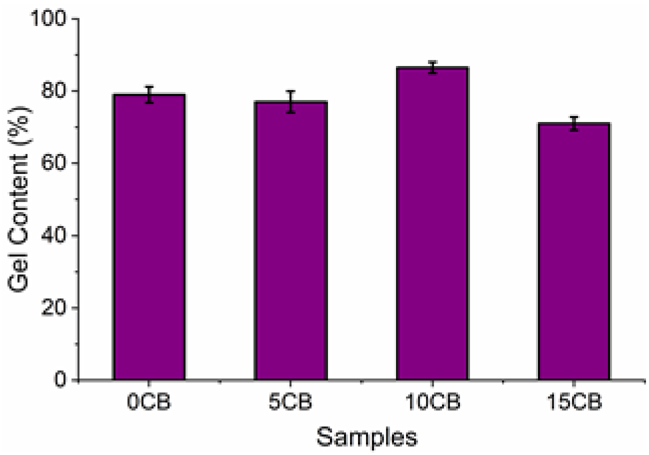

Figure 5. Gel content of EPDM and EPDM/CB composite materials

Figure 5 shows the effect of the amount of CB used as a bio-based filler on the swelling ratio of EPDM composites. Swelling ratio analysis also gives information about the gel content of the rubber material. The higher the gel content of the rubber material, the less water it absorbs into its structure and the less it swells. As seen in Figure 6, the swelling ratio of the samples decreased with the addition of CB. The highest swelling ratio was reached in the CB15 sample and about 180%, while the lowest swelling ratio was calculated as 105% in the CB10 sample.

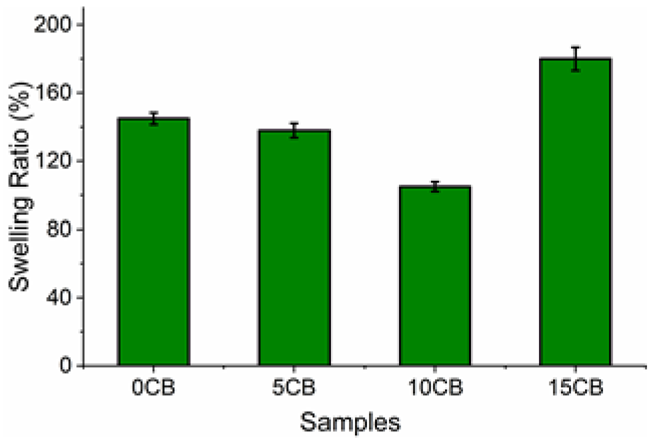

Figure 6. Swelling ratio values of EPDM and EPDM/CB composite materials

According to the gel content and swelling ratio analysis results, it was understood that the sample with the highest crosslink density was the CB10 sample using 10 phr CB. Gel content and swelling ratio analysis also support each other. In addition, the results of the crosslink density analysis are also compatible with the mechanical analysis results. Accordingly, composite material with high crosslink density and mechanical properties was synthesized by using 10 phr CB. The mechanical properties of the material have also decreased considerably due to the reduced crosslink density with the use of 15 phr CB.

4. Conclusion

Carbon black, which is one of the filler materials frequently used in the rubber industry, is a very harmful material in terms of both the environment and employee health, despite the superior mechanical properties it provides. For this reason, many research is carried out on the use of bio-based fillers to replace carbon black or to reduce the carbon black used per unit of rubber weight. The selection of bio-based filler materials, especially the selection of waste products, provides a great advantage with regard to both economic and sustainable environments. Herein, as a result of the production of cumin black oil, which is frequently used and consumed in our country, the waste cumin black pulp was added to the EPDM matrix at different weight ratios as a bio-based filler material. The effect of added CB particles on the rheological, mechanical and chemical properties of the produced composite material was investigated. MDR analysis shows that CB added up to 10phr increases the torque values and t_{s2} time of the material and decreases the t_{90} time. From the mechanical analysis results, it was understood that the EPDM sample (CB10) containing 10 phr CB was the optimum sample considering the tensile strength, elongation at break and toughness values. In addition, both the gel content and swelling analysis results are in accordance with the rheological and mechanical analysis results and show that the sample with the highest crosslink density in both analyzes is EPDM containing 10 phr CB. As a result of the characterization studies, it is evaluated that the waste CB can be used as a bio-based filling material in EPDM and rubber materials. The use of waste materials such as CB as filling material in the rubber industry is a very important gain in terms of both economic and environmental pollution.

Conflicts of interest

The authors declare no conflicts of interest.

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