Available online at www.dergipark.gov.tr

INTERNATIONAL ADVANCED RESEARCHES
and
ENGINEERING JOURNAL

Journal homepage: www.dergipark.gov.tr/iarej

e-ISSN: 2618-575X

International Open Access

Volume 02
Issue 02

August, 2018

Research Article

Investigation of using shelf-life passed milk in EPDM as bio-based filler

Ahmet Güngör [a], ***İsmail Kutlugün Akbay*** [a,*]

[a] *Mersin University, Chemical Engineering Department, 33343, Yenişehir/Mersin*

ARTICLE INFO

Article history:
Received 27 February 2018
Revised 08 June 2018
Accepted 11 June 2018

Keywords:
Bio-based polymers
Rubber
Shelf-life passed milk
Waste management

ABSTRACT

Waste management of dairy products is an important topic for both economic and environmental aspects. In order to remove or reduce the harmful effects of carbon black used as a filler material, the effects of polymers obtained by using some biological wastes such as shelf-life passed milk instead of carbon black on the physical and mechanical properties of ethylene propylene diene monomer (EPDM) rubber have been investigated. Moving Die Rheometer and Soxhlet extraction tests were applied to the obtained compound and the results were evaluated. MDR test results showed that the scorch time of the samples increased by 10% SP filler, and Soxhlet test results were in line with MDR test. Mechanical analysis showed that the addition of casein polymer improved the elongation at break values of the samples. The tests were concluded that the best resulting sample is 10% SP. FTIR result shows that the casein polymer is chemically bonded to the EPDM rubber. The results showed that the prepared bio-based filler could be used as an alternative and non-hazardous filler.

1. Introduction

Ethylene propylene diene rubber (EPDM) is one of the most widely used synthetic rubber types containing ethylene, propylene and diene monomer. EPDM have been used for many years for the applications of rubber ignition switches, underfloor heating, electromagnetic noise protection, electronic and electrical applications wire, sports equipment, outdoor electrical insulators [1]. The diene part of EPDM shows excellent resistance to thermal and electrical properties. Low price, good mechanical properties, good radiative protection, high filler capacity and chemical resistance are the main reasons for the use of EPDM in many areas [2, 3].

The mechanical, thermal and rheological properties of EPDM can be changed by the molecular weight of the rubber and the filler used. Filling material is used in vulcanization process for rubbers in order to obtain the desired mechanical and thermal properties [4]. In this context, the chemical interactions between the EPDM and the filler materials and the homogeneous dispersion of the filler material in the polymer matrix have a significant effect on the ultimate mechanical, thermal and rheological properties of the material matrix [5, 6].

Carbon black (CB) is the most important filler material for rubber and is widely used. It is also used as a colouring agent in the rubber industry due to its chemical and thermal stability [7]. Despite the use of many areas, long term exposure to carbon black is extremely harmful to the health of workers in the rubber industry. In addition, the carbon black used often has a tendency to clump in the material, and agglomeration is often problematic in terms of material [8]. To overcome these disadvantages is to increase the production of biodegradable and biodegradable polymer composites. In addition, the use of biodegradable and biodegradable polymeric materials as a filler material may potentially reduce dependence on fossil fuel products. It is important to note that producers always look for cheaper alternatives that do not reduce mechanical and other properties [9, 10].

In the world, economic development and transformation in recent years has also affected production, consumption and trade of milk and dairy products. Especially in developing countries, per capita income and the increase in population have increased the consumption of milk and dairy products, which is a compulsory food item and occupies an important place in human nutrition [11]. This increase in demand for milk and milk products has also

* Corresponding author. Tel.: *+ 90 (324) 3610001 - 7390*.
E-mail addresses: *ahmet.gungor@mersin.edu.tr* , *akbay@mersin.edu.tr*

led to an increase in the production and trade of milk and dairy products and has contributed to the transformation of the dairy and dairy sector into a market that attracts national and international investments, especially in developing countries. The production / consumption of milk and milk products in our country also shows a rapid increase [12]. Parallel to this development, the amount of milk that has shelf-life passed milk is increasing day by day. Milk and dairy products that shelf-life passed are used and assessed in many milk powder, cheese, yeast, paint, glue and etc. areas [13].

There is no study regarding the usage of biobased filler obtained from shelf-life passed milk, but in the literature, there is a growing interest to use biobased fillers in different polymers and rubbers. Barczewski et al. [14] studied chestnut shell waste within poly(lactic acid). The modulus values of the sample were significantly increased with the addition of chestnut shell. Unfortunately, mechanical properties of the samples were decreased with the addition of bio-filler. Patil et al. [15] reported fly ash within chitosan composites for the purpose of filler in matrixes. The fly ash wastes were modified with a non-ionic surfactant and the final material were obtained with smooth surface and spherical shape. The addition of fly ash wastes was increased the mechanical properties. Sareena et al. [16] worked on peanut shell powder as a bio-based filler in natural rubber. The addition of the filler has increased the mechanical properties regarding to pristine natural rubber, the morphological analysis showed that the 10 phr loading was the best resulting sample. Li et al. [17] studied the examination of the effects of altering the properties of rice bran carbon (RBC) within nitrile rubber (NBR). The addition of RBC has improved the mechanical properties of composites.

In this study, the effect of the casein polymer obtained from the shelf-life passed milk on the physical and mechanical properties of ethylene-propylene-diene ter monomer (EPDM) rubber was investigated. Characterization tests such as MDR (Moving die rheometer), elastic modulus, elongation at break and cross-link density were performed to observe the effects of the bio-filler material used on the EPDM rubber at different percentages and to observe the effects of these bio-based polymeric materials on the EPDM rubber.

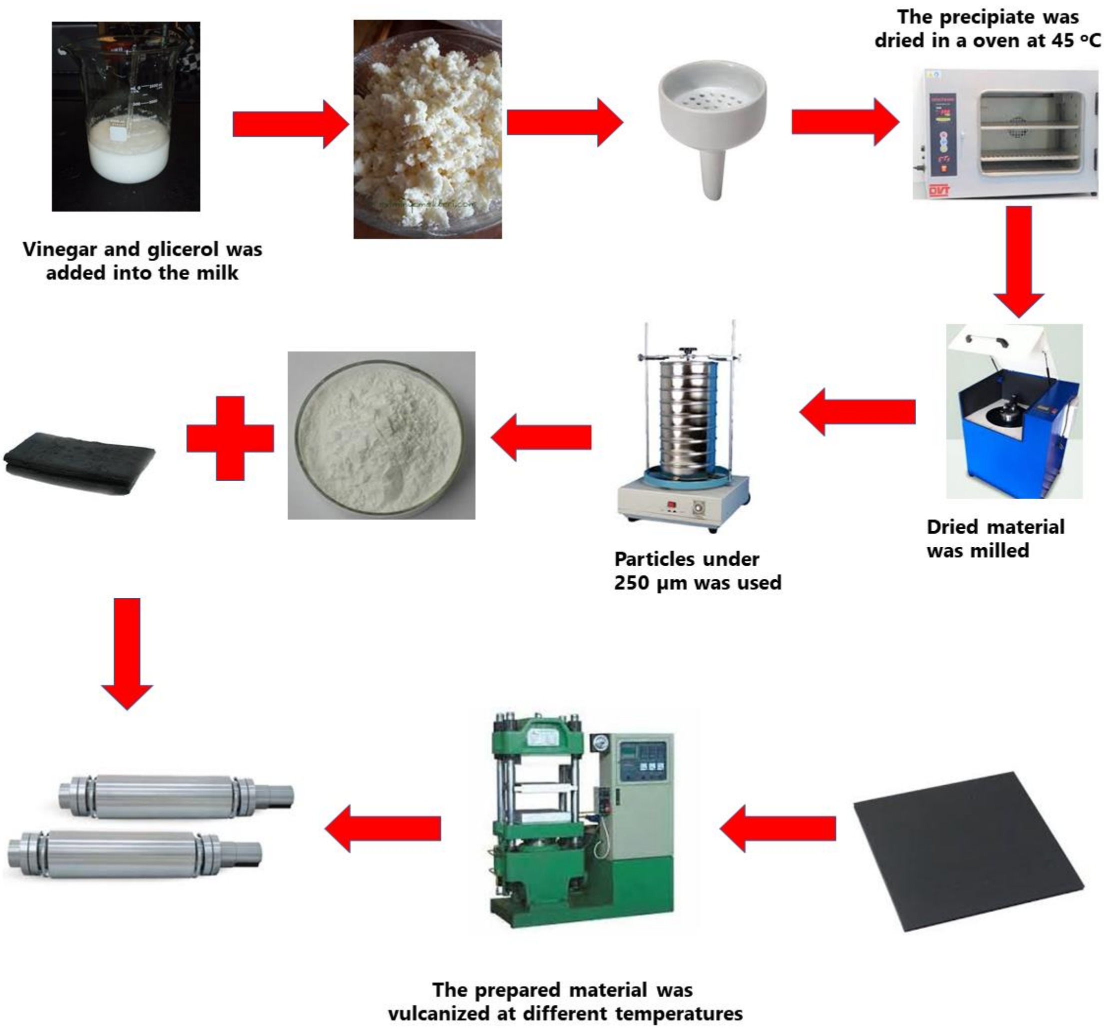

Figure 1. Schematic Representation of Sample Preparing

2. Material & Method

TAC / 50, peroxide, casein polymer obtained from shelf-life passed milk (biologically based polymeric filler), glycerine (cross-linker in casein polymerization), vinegar, EPDM rubber, mineral oil, stearic acid, zinc oxide and carbon black were used in the study.

The materials were taken in the amounts indicated in Table 1 and mixed in a Kneader-type closed mixer (Baihong mark ML-132 model) until they became mixed and rubber mixing was obtained. The mixing was taken from the internal mixer. The prepared mixing was shaped through a two-roll mill (Baihong mark HL-66 model) to obtained a 2 mm-thick EPDM sheet. The prepared EPDM sheet was placed in 15x15 mm mould and vulcanized at 172,15 ° C, 20 MPa pressure and 5 minutes in a laboratory type heat press.

Table 1. The formulate of the rubber mixing

Materials	Amount (phr)
EPDM Rubber	100
Carbon Black	100
Mineral Oil	82
Zinc Oxide	5
Stearic Acid	1,5
TAC/50	2
Peroxide	7
Casein Polymer (SP)	5, 10, 15 % (w/w)

2.1 Obtaining Casein Containing Biopolymeric Material from Complete Shelf Life

500 mL milk was added to the beaker and heated to boiling on a magnetic stirrer. After it was boiled, 125 mL Tariş mark vinegar (5-6 % acetic acid v/v) was added to the milk and glycerine (as crosslinker) was added in different amounts. Sometime later, the milk started to viscose and precipitate. The resulting precipitate was filtered using a Buchner funnel. The filtered precipitate was dried for 45 minutes at 50 ºC and the dried sample was ground to a ball mill. The bio polymeric material, whose particle size has been reduced and homogenized, has been added into the rubber at certain ratios. The schematic representation of the sample preparing is given in Figure 1.

2.2 Tests and Analyses Applied to the Samples

Various characterization studies have been carried out to test the mechanical, rheological and chemical properties of EPDM. For the characterization studies, the Perkin Elmer ATR-FTIR device was used to investigate the chemical altering of the samples. The MDR type rheometer (Montech mark MDR 2000) was used to understand the vulcanization kinetics of the process. The Soxhlet extraction was used for the determination of the cross-linking ratio and after the addition of the bio polymeric material.

Tensile breaking test was performed on specimens cut into 'Dogbone' according to ASTM D412 standards by applying a force of 50 mm per minute in Shimadzu AGS-X Tensile Testing Machine tester. Samples taken from rubber compound containing biopolymeric material at various ratios were vulcanized for 5 and 10 minutes at 172,15 ° C in the MDR 3000 Basic to determine their rheological properties. The Cure Rate Index (CRI) formula [18] was used to examine the MDR results in Equation 1.

$$\mathrm{CRI} = 100/(t_{90} - t_{s2}) \quad (1)$$

Where t_{90}; represents the optimum vulcanization time, and t_{s2} represents the scorch time of the material.

In the Soxhlet Extraction analysis, it is intended to dissolve the non-cross-linked portions of the suspended materials in the solvent (hexane), measure the amount of remaining mass, and thus find the cross-linking percentage. In this direction, certain weighted materials were applied on a Soxhlet extraction for 24 hours. Crosslink ratio [19] of the samples was calculated in Equation 2.

$$\text{Crosslink Ratio} = W_f/W_i * 100 \quad (2)$$

Where, W_f; represents the final weight, W_i represents the initial weight.

3. Results

3.1 Effect of Crosslinker Quantity on Vulcanization Parameters

Glycerine was used as a cross-linking agent in the synthesis of shelf-life passed milk to casein polymer. Prior to casein synthesis, different amounts of glycerine were used to optimize the amount of cross linker to be used and polymerization was carried out. The synthesized bio polymeric material was added into the EPDM to study the effect of the amount of cross linker on the vulcanization parameters and the torque curves are plotted in Figure 2. Also, the vulcanization parameters are given in Table 2. According to the results of MDR analysis, t90 values were not affected by the glycerol amount added for the polymerization process, while an increase in ts2 was observed in proportion to the amount of glycerine added. From the results obtained, the optimum amount of cross-linker in shelf-life passed milk to casein polymerization was found to be 0.5 mL glycerin, and in the subsequent runs biopolymeric material produced with 0.5 mL glycerine was used for the remaining studies.

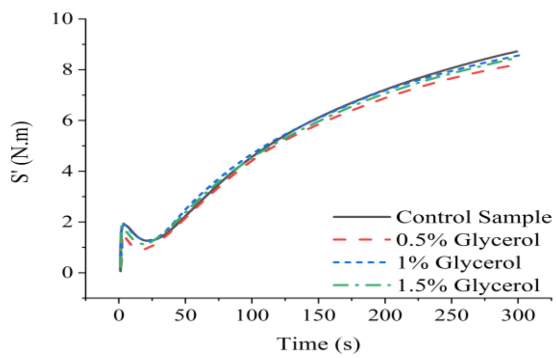

Figure 2. MDR results of bio polymeric materials produced with different cross linker quantities

Table 2. Effect of Cross-linker ratios on parameters

Sample	t_{s2} (min)	t_{90} (min)	CRI
SP (0.5 mL)	0.58	3.54	33.67
SP (1.0 mL)	0.59	3.58	33.44
SP (1.5 mL)	1.01	3.59	28.13
Control	1.05	4.00	33.89

3.2. Mechanical Test Results

The mechanical test results of the EPDM samples with different amounts of casein polymer are shown in Figure 3. When the graph showing the elastic modulus values was examined, the highest elastic modulus value was observed in the EPDM rubber (control sample) without casein polymer (SP) obtained from the milk. The elastic modulus values of SP-containing specimens as well as the Neat EPDM sample give very close results. For further analysis, EPDM rubber with 20% SP was prepared but the polymer was not homogeneously mixed with the EPDM paste. That is, the EPDM rubber has become overwhelmingly saturated with the casein polymer and a certain amount of polymer dumps into the surface of the samples prepared. For this reason, 20% SP containing EPDM rubber analysis were not applied.

In the graph showing elongation values, it was determined that the optimum composition is EPDM containing 10% SP. A reduction in the amount of elongation is observed in the EPDM pulps with a weight percentage of 10% SP. This may be thought to be due to increased surface interaction between the casein polymer produced from the shelf-life milk and the EPDM rubber.

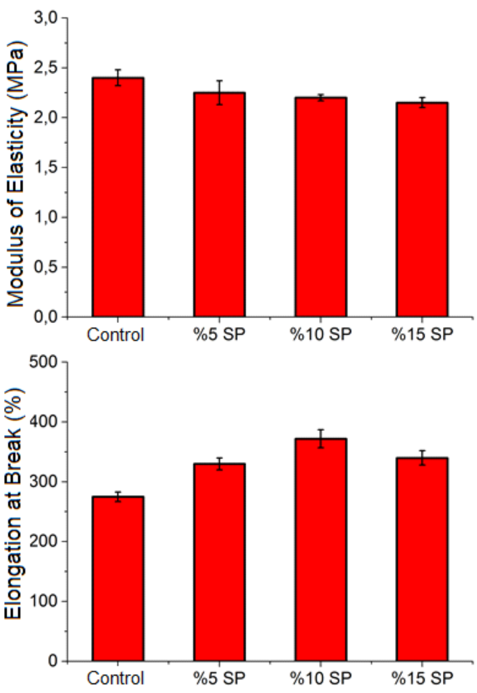

Figure 3. Mechanical test results of samples

3.3 MDR Results

The vulcanisation parameters of the EPDM samples prepared using the SP in the proportions are given in Table 3 and the torque curves in Figure 4. As can be seen from Table 3, it is seen that EPDM mixtures (control sample) with t_{90} and t_{s2} values and EPDM mixtures containing 5% and 10% SP give similar results and in this context, the CRI values are very close to each other. However, when the SP rate is increased to 15%, it is seen that the mentioned values have decreased remarkably. This resulted in a significant reduction in the CRI value of the sample containing 15% SP, which is in agreement with the results of the mechanical test.

The findings were parallel to the mechanical results of the materials for all samples. As a result, an EPDM sample containing 10% SP was selected as the optimum additive ratio based on both the mechanical data and the vulcanization parameters.

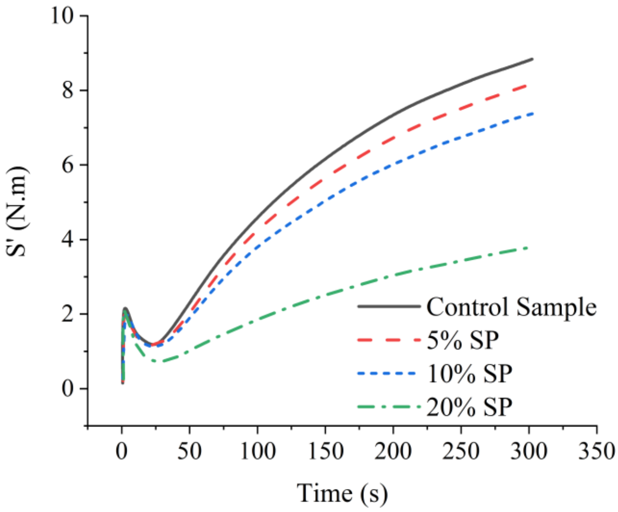

Figure 4. Comparison of MDR test results for different compounds

Table 3. Comparison of MDR test results for different compositions

Sample	t_{s2} (min)	t_{90} (min)	CRI
Control	1.05	4.00	33.89
% 5 SP	1.08	4.02	34.01
% 10 SP	1.14	4.03	34.60
% 20 SP	2.53	7.24	21.23

3.4. Soxhlet Test Results

The addition effect of casein polymer obtained from the shelf-life passed milk is shown in Table 4, which contributes very little to the formation of cross-linking in the added EPDM rubber matrix. When the amount of SP added to the EPDM rubber had a composition of more than 10%, a decrease in cross-linking was observed as a result of the analysis carried out. For the case of samples containing over SP of 10%, the migration started to take place. The highest crosslinking ratio was calculated as EPDM with 10% SP. The findings are consistent with both mechanical and rheological test results.

Table 4. Cross-linking ratios

Sample	Crosslinking Ratio(%)
Control	76.56 ± 0.08
% 5 SP + EPDM	77.75 ± 0.12
% 10 SP + EPDM	80.23 ± 0.05
% 15 SP + EPDM	75.69 ± 0.15

3.5. FTIR analysis

The Neat EPDM has not got a molecular structure (C = O). However, in the FTIR analysis, which is given in Figure 5, of EPDM rubber containing 10% SP, a peak at 1745 cm^{-1} wavelength that represent the characteristic peak of casein polymer is observed [18]. This result shows that the casein polymer is chemically bonded to the EPDM rubber.

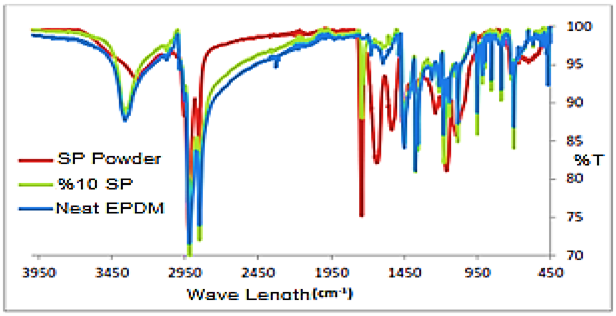

Figure 5. FTIR analysis results

3.5. Replacing Carbon Black with Casein Polymer

In the previous stages of the study, the amount of carbon black in the produced EPDM samples was 30 phr according to the formulation given in Table 1. However, in this section, the amount of carbon used reduced as 30 phr to reduce the effect of carbonaceous filler, which is carcinogenic and harmful to health, is gradually reduced with casein biopolymer obtained from shelf-life passed milk and EPDM samples is prepared accordingly. The torque curves of the prepared EPDM samples are shown in Figure 6 and the vulcanization parameters are shown in Table 5. When Figure 6 is examined, the casein polymer obtained from the shelf-life passed milk is mixed in EPDM rubber at different ratios, the maximum and minimum torque values are decreased according to the control sample of the material. Considering the CRI values, it is seen in Table 5 and Figure 6 that close results are obtained with the control sample and that the EPDM rubber with 20 phr carbon black + 10 phr SP gives similar results to the control sample. It was observed that the increase of SP amount increased the t_{90} value, whereas, the value of t_{S2} seems to be extended as an undesirable result. For this reason, EPDM rubber with 20 phr carbon black + 10 phr SP was chosen as the optimum compound.

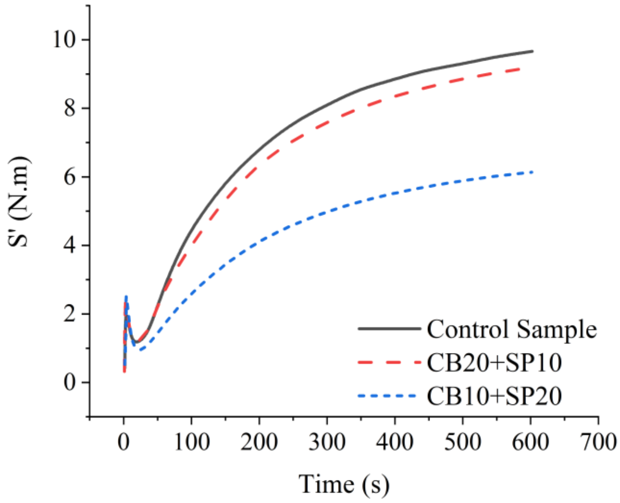

Figure 6. Examination of carbon in-effect by MDR test

Table 5. Comparison of the carbon effect

Sample	t_{s2}(min)	t_{90}(min)	CRI
CB10+SP20	0.74	3.50	36.24
CB20+SP10	0.54	3.22	37.30
Control	1.05	4.00	33.89

4. Suggestions and Discussion

In this study, casein polymer obtained from shelf-life passed milk was used for the disposal of waste as well as for reducing the carbon content in EPDM rubber. First, the casein polymer is synthesized from shelf-life passed milk and the mechanical, chemical and vulcanization properties of the final material obtained by adding EPDM rubber to certain ratios have been investigated. Analysis by mechanical tests and Soxhlet extraction showed that the addition of polymer obtained from the shelf-life passed milk increased the strength of the EPDM rubber. The results showed that the most suitable composition is the EPDM containing 10% SP. In the MDR analysis, the rheological properties were improved by the addition of the polymer obtained from the shelf-life passed milk. It has been determined that the obtained polymer can be used as a filler material in EPDM rubber and as a result of the analysis made, it is understood that polymers that made by shelf-life passed milk can be used instead of carbon black fill in EPDM rubber and it can reduce harmful effects to health of people and the environment.

Nomenclature

SP : Casein polymer obtained from shelf life finished milk

CB : Carbon Black

phr : Per Hundred Rubber

CRI : Cure Rate Index

EPDM : Ethylene propylene diene rubber

MDR : Moving Die Rheometer

References

1. Ozdemir, T., A. Gungor, and I. Reyhancan, *Flexible neutron shielding composite material of EPDM rubber with boron trioxide: Mechanical, thermal investigations and neutron shielding tests.* Radiation Physics and Chemistry, 2017. **131**: p. 7-12.
2. Ravishankar, P., *Treatise On Epdm.* Rubber Chemistry and Technology, 2012. **85**(3): p. 327-349.
3. Yasin T, Khan S, Nho Y-C, Ahmad R., *Effect of polyfunctional monomers on properties of radiation crosslinked EPDM/waste tire dust blend*. Radiat Phys Chem,2012. **81**: p. 421–425.
4. Ozdemir, T., et al., *Neutron shielding of EPDM rubber with boric acid: Mechanical, thermal properties and neutron absorption tests.* Progress in Nuclear Energy, 2016. **89**: p. 102-109.
5. Cavdar, S., T. Ozdemir, and A. Usanmaz, *Comparative study on mechanical, thermal, viscoelastic and rheological properties of vulcanised EPDM rubber.* Plastics Rubber and Composites, 2010. **39**(6): p. 277-282.
6. Alex S. Sirqueira, Bluma G. Soares, *The Effect of Functionalized Ethylene Propylene Diene Rubber (EPDM) on the Kinetics of Sulfur Vulcanization of Normal Rubber/EPDM Blends.* Macromolecular Materials and Engineering, 2007. **292**(1): p. 62-69.
7. Accorsi, J. And E. Romero, *Special Carbon-Blacks for Plastics.* Plastics Engineering, 1995. **51**(4): p. 29-32.
8. Niranjan, R, Thakur, A.K. *The toxicological mechanisms of environmental soot (black carbon) and carbon black: Focus on Oxidative stress and inflammatory pathways.* Frontiers in Immunology, 2017. **8:** p 1-20.
9. Burmistrov, I., et al., *Improvement of carbon black based polymer composite electrical conductivity with additions of MWCNT.* Composites Science and Technology, 2016. **129**: p. 79-85.
10. Martinez, L., et al., *Influence of friction on the surface characteristics of EPDM elastomers with different carbon black contents.* Tribology International, 2011. **44**(9): p. 996-1003.
11. Flint, S. and N. Hartley, *A modified selective medium for the detection Pseudomonas species that cause spoilage of milk and dairy products.* International Dairy Journal, 1996. **6**(2): p. 223-230.
12. Akbay, I. and T. Ozdemir, *Monomer migration and degradation of polycarbonate via UV-C irradiation within aquatic and atmospheric environments.* Journal of Macromolecular Science Part a-Pure and Applied Chemistry, 2016. **53**(6): p. 340-345.
13. Kinsella, J.E. *Milk proteins: Physicochemical and functional properties.* C R C Critical Reviews in Food Science and Nutrition. 1984, **21**(3): p. 197-262.
14. Barczewski M, Matykiewicz D, Krygier A., *Characterization of poly(lactic acid) biocomposites filled with chestnut shell waste*. J Mater Cycles Waste Manag, 2017. **20**:2: p. 914-924
15. Patil AG, Poornachandra S, Gumageri R., *Chitosan composites reinforced with nanostructured waste fly ash,* J Mater Cycles Waste Manag. 2017 **19**: p. 870–883.
16. Sareena C, Ramesan MT, Purushothaman E., *Utilization of peanut shell powder as a novel filler in natural rubber*. J Appl Polym Sci 2012. **125**: p. 2322–2334
17. Li M-C, Zhang Y, Cho UR., *Mechanical, thermal and friction properties of rice bran carbon/nitrile rubber composites: Influence of particle size and loading*. Mater Des 2014. **63**: p.565–574
18. Essawy, H, El-Nashar, D. *The use of montmorillonite as a reinforcing and compatibilizing filler for NBR/SBR rubber blend.* Polymer Testing 2004. **23**(7): p. 800-807
19. Xiao, C, Zhou, G. *Synthesis and properties of degradable poly(vinyl alcohol) hydrogel.* Polymer Degradation and Stability, 2003. **81**(2): p. 297-301.
20. Guo, M. and Wang, G, *Milk Protein Polymer and Its Application in Environmentally Safe Adhesives.* Polymers, 2016. **8**(324): p. 1-12.