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The Effect of Plant-Based Oils and Cellulose Fillers on The Rheologicaland Physico-Mechanical Properties of Tire Tread

Anıl Alkan[1], Alev Akpinar Borazan[1]*

Abstract: In this study, commercial tire tread which should be as an economical and more environmentally friendly was aimed to be modified by using cellulosic fiber and/or plant-based oil.The ratio of cellulose fiber (from the waste chestnut shell, the waste pistachio shell and pinecone) to carbon black in the manufacture of tire's tread was used as 0.33:1. Three plant-based oil (canola, corn and sunflower oil) used as 20.8 phr instead of the aromatic oil in the mixture of the tire's tread. The tire treads were prepared by using 10 different mixture, one of them was control and others testing mixture. Rheological tests before vulcanization and physico-mechanical tests (tensile strength, elongation at break, tear strength, 300% modulus, hardness, abrasion, density) after vulcanization were applied to these prepared mixtures. Vulcanization characteristics were obtained by using a moving die rheometer (190°C,3min); minimum torque, maximum torque, cure rate, the scorch and cure time of the prepared rubber mixture. All tests were carried out in accordance with the relevant ASTM D standard test procedure.According to the test results, the rheological, physical and mechanical properties showed significant changes depending on the natural fillers. The values of the curing time and scorch time were increased while the maximum and minimum torque values were reduced for rubber samples produced using plant-based oil and/or cellulose fiber.Plant-based oil had higher cure extent values than the cellulose fiber this represents a higher cross-linking degree during cure reaction. The measured values of the abrasion and tensile strength were reduced negatively with all types of cellulose fillers. Test results of all of the different types of Plant-based oil were proper in standard values except tear strength.

Keywords: Cellulose fiber, Plant-basedoil, Physico-mechanical, Rheologicalproperties, Tire tread

Introduction

Today, rubber materials are located in many areas of our lives.The rubber industry in the world can be constantly made innovations because of the properties of rubber; easily processability, availability in different application areas, and usability as a semi-processed product. These are all the preferred properties for any manufacturing material in this market (Öter et al. 2011; Namazi 2017).
In the world, the waste of rubber materials especially in the form of used tires caused to the serious environmental problem due to their very complex structure and composition, this increases year by year. Many countries have changed in their policy or legislated to prevent this situation and to protect the environment (ETRMA 2013; Garciaet al.2017; Sienkiewicz et al. 2017). Rubber material essentially is consisting of the rubber, the reinforcing fillers, the process oils, and additives. The mechanical and rheological performance of rubber materials are changeable with the filler loading, the dispersing quality of fillers and the other additives (Sobhy et al. 2003; Öter et al. 2011).Since January 2010, highly aromatic oils

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including PAH were banned according to a European Directive, to avoid contaminating the environment (ETRMA 2013).Some researchers and manufacturers have turned to plant-based oils and other natural tire ingredients to reduce cost, and increase the sustainability of the tire (Öter et al. 2011; Saxena 2011; Chokan and Sombat et al. 2014; Zanchet et al. 2016).

The subject covered in this study is the determination of the physicomechanical and rheological behavior of rubber blends for the tire tread affected by cellulosic fibers and/or plant-based oils.

The original aim is to reduce the cost of rubber blends and improve the tire properties, but the main advantage of selected fillers is that it allows them to focus on forwarding sustainability.

Material and Method

The cellulose fibers were obtained from the waste chestnut shell, the waste pistachio shell and pinecone with the end of some processing. The ratio of cellulose fiber to carbon black in the manufacture of tire's tread was used as 0.33:1. Three plant-based oils (canola, corn and sunflower oil) were provided from local suppliers in Turkey. They were used as 20.8 phr instead of the aromatic oil in the mixture of the tire's tread. The tire treads were prepared by using 10 different mixture, one of them was control (RC) and others testing mixture. The chemical compositions and quantities of all additives used in the production of commercial tire tread (RC) given in the Table 1. is subject to the confidentiality agreement with the company.

Table 1. Alternative formulation of tire treads

Codes of the Tire tread / Function/ Compounds	RC	R1	R2	R3	R4	R5	R6	R7	R8	R9
	Amount (phr)									
Matrix										
Rubber Blend (Natural &Butadien Rubber Mix)	100	100	100	100	100	100	100	100	100	100
Filler										
Carbon Black (N330)	66.67	50	50	50	66.67	66.67	66.67	66.67	50	50
Alternative; Cellulose fiber filler										
pinecone	----	16.67	----	----	----	----	----	----	16.67	----
chestnut shell	----	----	16.67	----	----	----	----	----	----	16.67
Pistachio shell	----	----	----	16.67	----	----	----	----	----	----
Chemicals										
Activator	4.41	4.41	4.41	4.41	4.41	4.41	4.41	4.41	4.41	4.41
Homogenizer	1.81	1.81	1.81	1.81	1.81	1.81	1.81	1.81	1.81	1.81
Antiozonant/Antioxidant	3.94	3.94	3.94	3.94	3.94	3.94	3.94	3.94	3.94	3.94
Process oil										
Distillate Aromatic Extract (DAE)	20.83	20.83	20.83	20.83	----	----	----	10.42	10.42	10.42
Alternative; Plant based oils										
Canola oil	----	----	----	----	20.83	----	----	----	----	----
Corn oil	----	----	----	----	----	20.83	----	----	----	----
Sunflower oil	----	----	----	----	----	----	20.83	10.42	10.42	10.42
Vulcanization agents										

Curing/vulcanizing agent	1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67
Activator/ Accelerator	1.77	1.77	1.77	1.77	1.77	1.77	1.77	1.77	1.77	1.77

Firstly, polymer mixtures were prepared as a master batch in an internal mixer by a laboratory two-roll mill (HMO Mak San Tic.Ltd.) with 2.5kg capacity and friction factor 1.1. The temperature of the mill did not exceed 95 °C and rotor speed was 5 rpm while working. Mixing procedure is given in Table 2.

Table 2.Mixing procedure of tire tread' compounds

Master batch	**Time(min.)**
Charge Rubbers	20-32
Filler & process oil &chemicals	10-15
Discharge mill	9-14
Final batch	
Master batch	10-15
Vulcanization agents	12-23
Discharge mill	10-19

The rheological properties of polymer samples were obtained by using a moving die rheometer (MDR, Gotech M2000A) at 190°C according to ASTM D 1646 standard. The values of t_{s2}, t_{90}, M_L, M_H were measured; cure extent and cure rate index (CRI) were calculated from the values according to Equation 1 and Equation 2, respectively.

$$\text{Cure extent} = M_H - M_L \qquad (1)$$

$$\text{CRI} = 100 / (t_{90} - ts_2) \qquad (2)$$

The vulcanization of polymer samples were carried out with a DEVOTRANS DVT NP Y sample preparation press at 170 °C under 15 MPa pressure for specified times which correspond to their t_{90}. From compression molded sheets (Figure 1.) specimens were prepared in required dimensions by standard to study the physico-mechanical properties of vulcanizates.

Figure 1. Scaling of the mold to standard blades (Akpinar Borazan, 2017)

Tensile strength, elongation at break, tensile modulus (300%) and tear strength were determined by using Tensile Testing Machine (DEVOTRANS-Dvt BE), according to ASTM D412. Both tensile and tear properties used a testing speed of 500 mm/min. The density of the vulcanized rubber samples were determined according to Archimedes Principle based on the ASTM D 297. DEVOTANS DVT DA 6 were used for measuring abrasion of the rubber vulcanizates, according to ASTM D 5963 Hardness of the vulcanized samples was determined according to ASTM D2240 by using a Shore A durometre.

After physico-mechanical tests, the surface morphology of some vulcanized rubber samples were examined under the scanning electron microscope (SEM., Zeiss Supra 40VP, Germany) at an acceleration voltage of 10kV.

Results

In this study, the effects and usability of plant based-oil and /or cellulose fiber on different tire tread compounds were evaluated.

For cure system crosslinking isotherms were given in Figure 2a.which was taken at 190°C for 3 minutes. The resulting scorch time, cure time, minimum rheometer torque and maximum rheometer torque were given in Figure 2b. for comparison cure system of polymer samples.

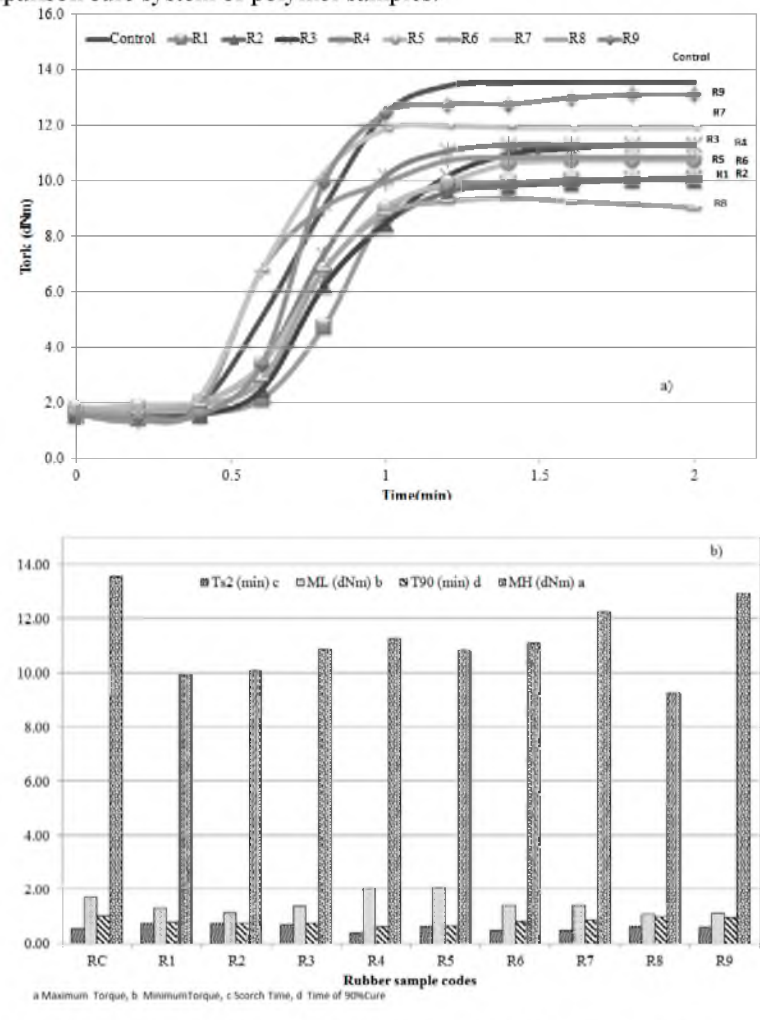

Figure 2. For all different rubber samples **a)** Crosslinking isotherms, **b)**Rheological properties

The values of the curing time(t_{90}) and scorch time(t_{s2}) were increased while the maximum (M_H) and minimum (M_L) torque values were reduced for rubber samples producedusing plant-based oil and/or cellulose fiber. Plant-based oil had higher cure extent values than the cellulose fiber this represents a higher cross-linking degree during cure reaction (Table 3.).Maximum rheometer torque, M_H, which is related to the stiffness of cured compound, is minimum for R8 with made of pinecone and sunflower oil.

Table 3. Cure characteristics

	RC	R1	R2	R3	R4	R5	R6	R7	R8	R9
Cure extent (dNm)	11.83	8.61	8.92	9.48	9.24	8.78	9.71	10.83	8.16	11.82
CRI (min-1)	8.45	11.61	11.22	10.55	10.82	11.39	10.30	9.24	12.26	8.46

When mechanical properties of the plant-based oil and cellulose fiber were compared eachother, plant-based oil, especially sunflower oil and the combination of sunflower oil with aromatic oil have shown similar test results with control samples (Figure 3.).

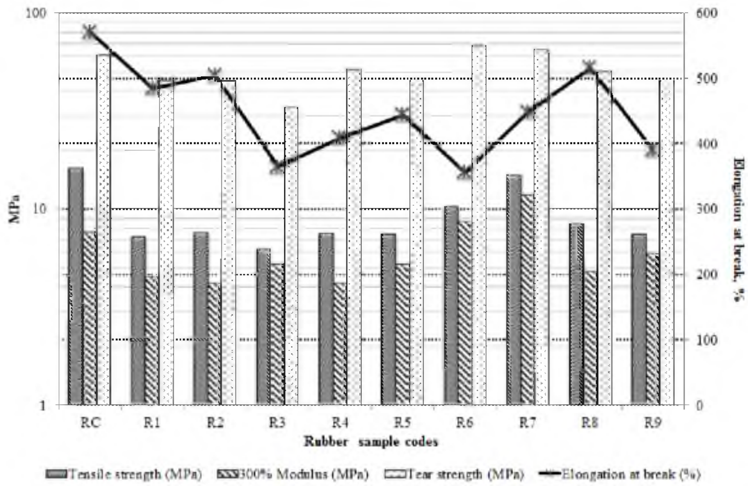

Figure 3. Effect of the cellulose fiber and/or plant-based oil fillers on some mechanical properties of tire treads

In vulcanizates containing sunflower oil (R6, R7) have been enhanced tensile strength, tear strength and modulus 300% values. On the other hand, it has been found that these properties were decreased when cellulose blend filler was added to the blends. Sunflower and pinecone fillers (R8) have better interaction than the sunflower and chestnut shell fillers (R9) were determined according to the test results of the mechanical properties of the tire tread.

Hardness valuesof the rubber samples were varying between 63 and 68.Plant-based oils were reduced hardness values in vulcanized rubber samples.

Figure 4.shows that the abrasion rate of vulcanized rubber samples (R1, R2 and R3) increases sharply with cellulose fiber filler. Abrasion resistance is usually affected by hardness, filler dispersion, and chemical structure of rubber.It has been determined that R7 has the highest abrasion resistance to the lowest abrasion in all vulcanized rubber samples.

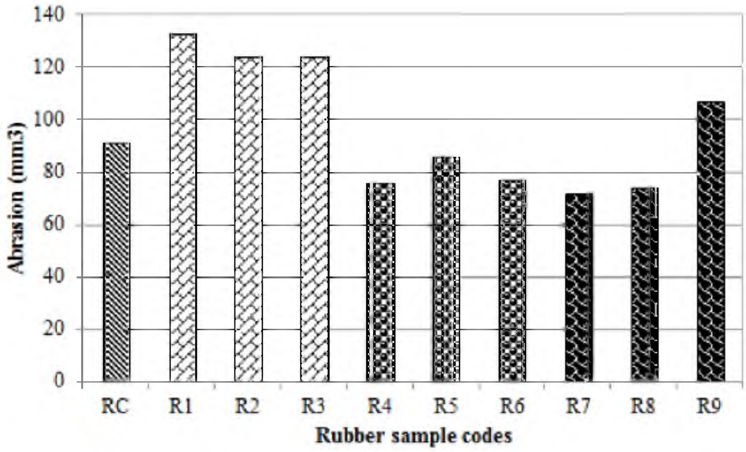

Figure 4. Effect of the cellulose fiber and/or plant-based oil fillers on abrasion of tire treads

SEM images of some vulcanized rubber samples are shown in Figure5. The dark backgrounds represent the rubber matrix and the bright parts are the fragments of additives which could not be dispersed homogenously.

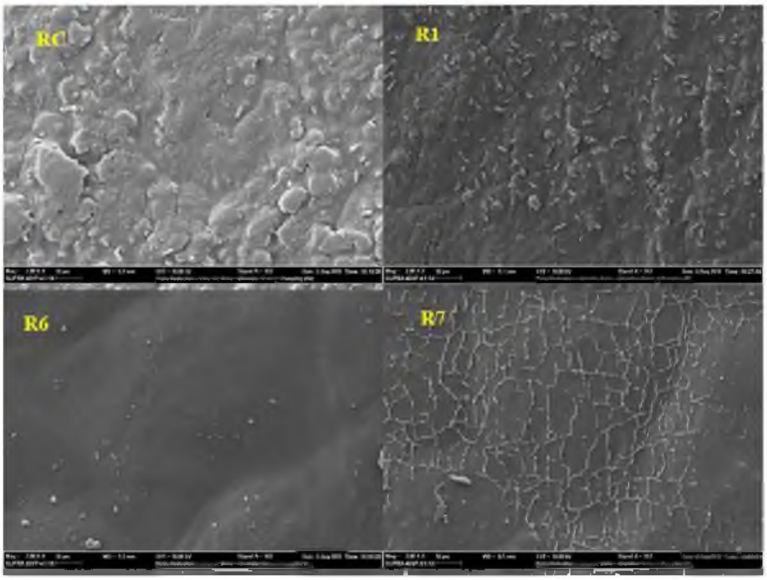

Figure 5. SEM image of thesurfacefromtherubbersamples at 2KX magnification.

A surfacemorphology of the pinecone fibers (R1) is shown (Figure 5.) where it can be observed that they are tubular with a circular section. The use of natural oils, as sun flower (R6 and R7) improves the dispersion and distribution of fillers in rubber samples.

The quality of the fiber–matrix interface is important when using natural fibers as reinforcement in the rubber matrix. Some physical and chemical methods are suggested to improve this interface. Physical treatment is the first step when used to natural fibers.This changes the structural and surface properties of the fibers but does not change the chemical compositions of them. At the later stage of this work, chemical treatment must be applied to the natural fibers before adding to the tire mixture.

Discussion and Conclusions

The experimental results showed that rheological properties of the tire tread after the substitution of aromatic oils with sunflower oil and substitution of carbon black with chestnut shell have not been deteriorated significantly.

Physical and mechanical properties of the vulcanizates were changed with natural filler.As a result of the experimental tests, cellulose fibres and plant based-oils are as alternative fillers for carbon black, aromatic oil that provides valuable data for manufacturers by small formulation adjustments.The further studies, especially plant-based oils can be compared with aromatic oil to make some required modifications in properties of physico-mechanical and rheological.

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References

Akpinar Borazan, A. (2017). Preparation and characterization of ethylene propylene diene monomer (EPDM) rubber mixture for a heat resistant conveyor belt cover, Anadolu University Journal of Science and Technology A- Applied Sciences and Engineering, 18(2), 507 – 520.

ASTM, Standard Test Method for Rubber Property—Abrasion Resistance (Rotary Drum Abrader), In ASTM Annual Book of Ame.Soc. for Testing and Materials Standards, Easton, MD, USA, D5963 - 15.

ASTM, Standard Test Method for Rubber Property—Durometer Hardness, In ASTM Annual Book of American Society for Testing and Materials Standards, Easton, MD, USA, D2240 - 15.

ASTM, Standard Test Methods for Rubber Products—Chemical Analysis, , In ASTM Annual Book of American Society for Testing and Materials Standards, Easton, MD, USA, D297- 15.

ASTM, Standard Test Methods for Rubber—Viscosity, Stress Relaxation, and Pre-Vulcanization Characteristics (Mooney Viscometer, In ASTM Annual Book of American Society for Testing and Materials Standards, Easton, MD, USA, D1646-15.

ASTM, Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers_Tension, In ASTM Annual Book of American Society for Testing and Materials Standards, Easton, MD, USA, D412-15.

Chokanandsombat, Y., Sirisinha, C. (2014). Influence of Aromatic Content in Rubber Processing Oils on Viscoelastic Behaviour and Mechanical Properties of Styrene-butadiene-rubber For Tyre Tread Applications. Polymers & Polymer Composites, 22(7), 599- 606.

ETRMA -EuropeanTyreRubberManufacturesAssociation, (2013). EuropeanTyreandRubberIndustry e Statistics. http://www.etrma.org/uploads/Modules/Documentsmanager/20131015---statistics-booklet-2013-final2.pdf (Accessed:18/07/ 2017).

Garcia, R., Vendrell, L., Mesas, M., Stan, F., Gheorghe, A., Ghenea, A., Spatzierer, L., Schweiger,S., Mattenberger, H. (2017) State of the art of waste prevention and management strategies in "urban-wins" countries and municipalities, https://www.urbanwins.eu/wp-content/uploads/2017/06/UrbanWINS-D1.1.-State-of-the-art-of-waste-prevention-and-management.pdf(Accessed:18/07/ 2016).

Namazi, H.(2017). Polymers in ourdaily life. BioImpacts, 7(2), 73-74.

Öter, M., Karaağaç, B., Deniz, V. (2011). Substitution of aromatic processing oils in rubber compounds. http://akademikpersonel.kocaeli.edu.tr/bkaraagac/sci/bkaraagac05.08.2011_14.57.35sci.pdf (Accessed: 05/06/2018).

Saxena, M., Pappu, A., Sharma, A., Haque, R., Wankhede, S.(2011) Composite Materials from Natural Resources: Recent Trends and Future Potentials, Chp 6, pp.121-162. Advances in Composite Materials -Analysis of Natural and Man-Made Materials, Dr. PavlaTesinova (Ed.), ISBN: 978-953-307-449-8, InTech, https://www.intechopen.com/books/advances-in-composite-materials-analysis-of-natural-and-man-made-materials/composite-materials-from-natural-resources-recent-trends-and-future-potentials
(Accessed: 25/04/2017).

Sienkiewicz, M., Janik, H., Borzedowska-Labuda, K., Kucinska-Lipka, J. (2017). Environmentally friendly polymer-rubber composites obtained from waste tyres: A review. Journal of Cleaner Production, 1(2017), 560-571.

Sobhy, M.S., El-Nashar, D.E., Maziad, N.A. (2003). Cure Characteristics and Physicomechanical Properties of Calcium Carbonate Reinforcement Rubber Composites. Egyptian Journal of Solids, 26(2), 241-257.

Zanchet, A., Garcia, P.S., Nunes, R.C.R., Crespo, J.S., Scuracchio, C.H. (2016). Sustainable Natural Rubber Compounds: Naphthenic Oil Exchange for another Alternative from Renewable Source. International Refereed Journal of Engineering and Science, 5(12), 10-19.