The Quality Properties of Tire Tread With Adding Filler of a Sunflower Oil and Pinecone Powder

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Abstract This study, aimed to be developed economical and environmentally friendly tires by modifying commercial tire tread using pinecone powder and sunflower oil. Different additives were used in the blend formulations: stearic acid as an accelerator and softener supplement, zinc oxide to increase the elasticity of the tread and provide abrasion and tear resistance, 40 MS was used to provide fluidity under high temperature and pressure. In the tread mixture, TMQ was preferred to resist aging, Ozone Wax to extend the life of the tire, and IPPD to provide flexibility under high temperature and pressure. Powder sulfur was used as a curing agent. 3 types of accelerators, DPG, CBS, and TMTD, were selected as chemical accelerators for curing time. Tire tread mixtures were prepared as a control formula and 7 different test mixture recipes. Rheological tests before vulcanization and physico-mechanical tests after vulcanization (tensile strength, elongation at break, tear strength, modulus 300%, hardness, abrasion, and density) were applied to all prepared mixtures. All tests were carried out in accordance with the relevant ASTM D standard test procedure. According to the test results, rheological and physic-mechanical properties showed significant changes depending on natural fillers.

Keywords: Pinecone powder, vegetable oil, physico-mechanical properties, rheological properties, tire tread

1. Introduction

The world population has reached 7.8 billion in 2020. Population growth continues despite many natural disasters and epidemics. Automobile sales worldwide reached approximately 64 million units in 2020, with an unstoppable increase like population growth. However, the industry has shown a downward trend due to Covid-19 and a slowing global economy. On the other hand, automobile demand and sales, which are indispensable to increase the living standards of even people living in countries with limited economy, and to meet the need for healthy and reliable individual transportation, have been revived in 2021 (ETRMA, 2013; Hu et al., 2014; Statista, 2021; OICA, 2021).

One of the most important issues to be considered during this time is that tires with a complex structure will generate large amounts of waste when they reach their expiry date and cause serious environmental problems. Many countries have changed their policies or put in place legal regulations to prevent this situation and protect the environment. Thus, a great deal of progress has been achieved in the sustainability management of waste tires that emerge when they reach the end of their life (ETRMA 2013; Sienkiewicz et al., 2017). Car tire mainly consists of rubber, reinforcing fillers, process oils and additives. Since January 2010, highly aromatic oils including PAH have been banned under the European Directive to avoid polluting the environment. For this reason, research has focused on the inclusion of more natural ingredients in tire mixtures, reducing the cost and ensuring an environmentally friendly approach. Natural vegetable oils will add value to low-cost agricultural raw materials if they are used as chemical additives or in the production of new products that show functional use potential for different purposes (Williams and Wool, 2000; Zhang et al.,2017). Different researchers have investigated and continue to investigate the addition of natural fibers in polymer matrices because of their biodegradability and many advantageous properties (Burgueño et al., 2005; Kalia et al., 2011): Low cost processing, low density, being easily supplied, etc. Properties of cellulose fibers evaluated in this group are affected by many factors such as variety, climate, harvest, maturity, shredding process applied, and fiber modification. In the studies carried out, the root, body, stem or leaves of many different cellulose sources such as flax, bamboo, sugar cane, Bagasse, Jute, Kenaf, Grass, Sisal, Hemp, Coconut, Banana peel, Ramie and Abaca, and the hard seeds or shells of some fruits have been processed (Lamy and Baley, 2000; Jahn et al., 2002; Miao, and Hamad; 2013; Pickering et al., 2016; Baghaei, and Skrifvars, 2020).

In this study, physico-mechanical and rheological changes occurring in the tread mixture by using sunflower oil and waste pine cone were investigated. By the work that is carried out, it is aimed to create an environmentally friendly tread mixture in addition to improving tread properties and reducing production costs.

2. Material and Method

Waste pine cone was subjected to drying and grinding processes and a cellulosic fibrous structure was obtained. Sunflower oil has been sourced from local suppliers in Turkey. 6 different recipes were created by using waste pine cones between 16 and 11 phr in tire tread mixtures. According to the result of our previous research regarding the effect of vegetable oils on the wheel dough mixture, sunflower oil was used as 10 phr in the recipes designed in this study (Borazan Akpinar and Alkan, 2019). The test results of 6 different recipes were compared with the test results of the control recipe (RC) that was prepared. The chemicals that are used in the tire tread mixtures and their quantities are shown in Table 1. Since the chemicals in the tire tread mixture are subject to the company confidentiality agreement, they are expressed according to their intended use.

The chemicals in the designed recipes were weighed in the specified proportions and turned into a rubber mixture in a two-cylinder laboratory type mill. Each recipe was prepared as 1.5 kg and the rotor speed was adjusted to not exceed 5 rpm and the mixture temperature was kept constant at 90 °C.

Table 1. The mixture designs for tire tread

Feeding materials and functions	Codes of the Tire tread and PHR						
	RC	R11A	R11B	R11C	R11D	R11E	R11F
Matrix							
Rubber Blend (Natural &Butadien Rubber Mix)	100	100	100	100	100	100	100
Filler							
Carbon Black (N330)	66.67	51	52	53	54	55	56
Alternative; Cellulose fiber filler							
Pinecone	----	16	15	14	13	12	11
Chemicals							
Activator	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
Antiozonant/Antioxidant	3.94	3.94	3.94	3.94	3.94	3.94	3.94
Process oil							
Distillate Aromatic Extract (DAE)	20.83	10	10	10	10	10	10
Alternative; Plant based oils							
Sunflower oil	----	10	10	10	10	10	10
Vulcanization agents							
Curing/vulcanizing agent	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

The mixing times of the mixtures prepared as master batch and final batch are shown in Table 2.

Table 2. Applied milling process to rubber and other components

	RC	R-11A	R-11B	R-11C	R-11D	R-11E	R-11F
Time to prepare master batch (min)							
Charge Rubbers	22	35	36	32	30	30	33
Filler & process oil &chemicals	10	20	20	23	24	22	19
Discharge mill	12	13	11	10	16	11	10
Time to prepare Final batch (min)							
Pre-mix t	10	15	15	15	20	15	14
Vulcanization agents	15	22	20	19	18	19	14
Discharge mill	15	21	18	17	18	16	19
TOTAL	84	126	120	116	126	113	109

The samples required for the tests were vulcanized in a laboratory cooking press (Devotrans A-130) for 7 minutes at 170 °C under 15 MPa pressure. The mold that is used to perform physico-mechanical tests according to the ASTM D standard and its dimensions are given in Figure 1.

In order to determine the vulcanization properties of each recipe sample and control recipe, according to ASTM D 1646 standard, using Rheometer device (MDR, Gotech M 2000A) for 3 minutes at a temperature of 190°, Scorch Time (T_{s2}, min), Time of 90% Cure (T_{90}, min), Minimum Torque (M_L, dNm), Maximum Torque (M_H, dNm), cure degree (dNm) and cure rate (CRI, min-1) values were determined. Rheological curing time (ΔT, min) has been determined using the difference between t_{c90} and t_{s2}

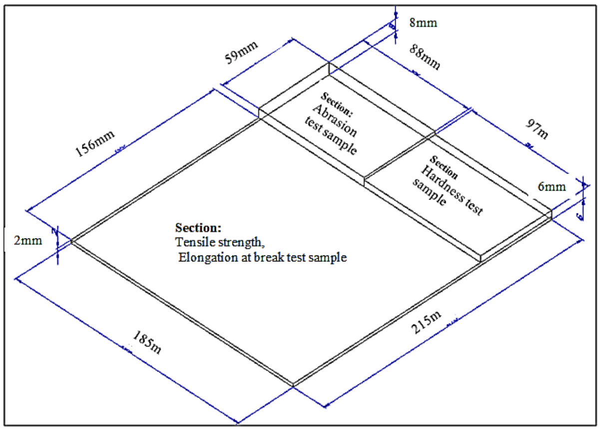

Figure 1. Test sample preparation mold design

3. Results and Discussion

In this study, 6 different tire tread mixes prepared using sunflower oil and waste pine cones were evaluated by comparing them with the results of the control recipe.

As seen in Figure 2, according to the rheological test results, the sunflower oil that is added to the recipe and the increasing amounts of cone fiber filling affected both the minimum and maximum torque values compared to the control recipe. While the maximum torque shows higher values than the control sample, although the minimum torque value increases with the increasing amount of pine fiber, a decrease was observed compared to the control sample. Accordingly, it has been calculated that the cure extent was increased and the curing rate (CRI) decreased.

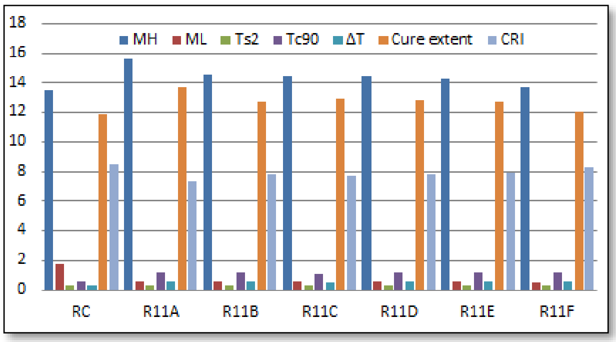

Figure 2. Effects of pinecone and sunflower oil on some rheological properties of the tire tread

It has been observed that when the pine cone waste powder is used as a reinforcing filler for HAF N-330 carbon black, this increases the rheological baking time ΔT. In our previous studies, it was determined that the use of pine cone waste powder alone as a filler in the mixture negatively affected the physicomechanical test values. For this reason, it has been found appropriate to be used as reinforcement in predetermined proportions with carbon black.

The results of the physico-mechanical tests are shown in Figure 3.

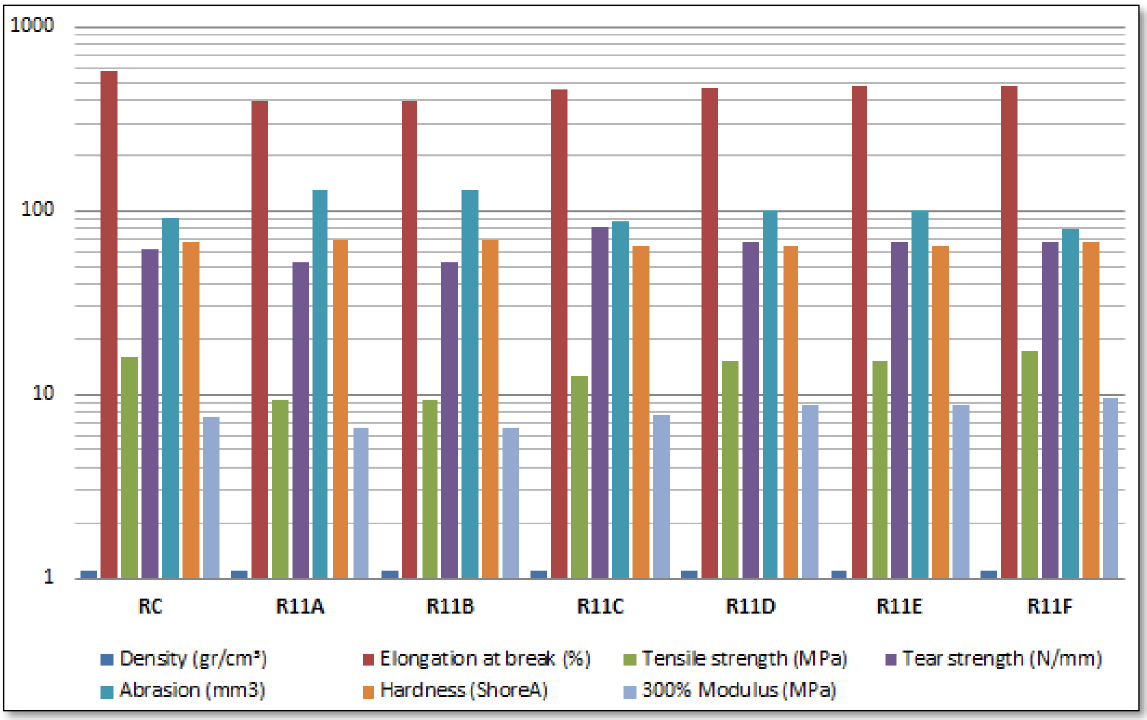

Figure 3. Effects of pinecone and sunflower oil on some physico-mechanical properties of the tire tread

11phr pine cone waste powder was used, and it was observed that the Tensile strength, Tear strength and 300% Modulus values of the samples were better than the reference recipe, but increasing the additional pine cone powder ratio reduced these values even more than the control sample. All recipes showed higher amounts of wear than the control sample except 11 phr, however, the hardness values varied between 67-70 Shore-A and did not present a significant difference.

4. Conclusions

The rheological and physicomechanical properties of the tire tread are enhanced by using sunflower oil partially instead of aromatic oil and using pine cone powder partially instead of carbon black.

The ability to use sunflower oil instead of aromatic oil offers an important alternative for tire manufacturers against legal regulations and ecological problems.

Although the use of carbon black is an important reinforcer in tire production, it also leads to an increase in costs during production. However, it has been determined that it is possible to partially use pine cone powder, which is sustainable, easily available and can be preferred as a cost effective replacement.

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