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Issue Article

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USE OF NEW EFFECTIVE LOCAL ANTIOXIDANTS FOR RUBBER MIXTURES AND STUDY OF CHEMICAL, PHYSICAL-MECHANICAL PROPERTIES

Abstract: *Microcrystalline paraffin raw material was used in the preparation of rubber compounds instead of Andioxidant SUNNOC raw material, and after all laboratory tests were positive, production testing was carried out. Studies have shown that the microcrystalline paraffin raw material improves the physical and mechanical properties of rubber compounds, has a positive effect on the aging process.*

In addition, the use of microcrystalline paraffin raw materials leads to lower cost and higher economic efficiency, which is why they are now being introduced and used in production.

Key words: *Microcrystalline paraffin, SUNNOC Antioxidant, 101-H and 101-L rubber compounds, standard formulation.*

Language: *English*

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Introduction

The Action Strategy for the further development of the Republic of Uzbekistan sets the task "Creation of technologies for obtaining import-substituting products from local raw materials and secondary resources". Our country needs to increase the number of local producers and increase the competitiveness of the raw materials they produce. According to the localization program in cooperation with the Tashkent Research Institute of Chemical Technology and the First Rubber Plant, LLC microcrystalline is a local import-substituting raw material to improve the physical and mechanical properties of rubber products, resistance to various external influences, wear and tear. Scientific and practical work has been carried out on the use of paraffin in place of imported antioxidant raw material SUNNOC. IN the present work, 2-propyl-, and 2-heptyl-, 1H-benzo[d]imidazole were prepared by condensation reaction of o-phenylenediamine with n-butanoic acid and n-octanoic acid, respectively. The prepared products were characterized by FT-IR, 1H-NMR spectroscopy and melting point. These products were incorporated into acrylonitrile butadiene rubber

(NBR) composites with two different fillers (Silica and High Abrasion Furnace carbon black HAF) as an antioxidant additive with different concentrations from 1up to 2 phr as a comparison with 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) as a traditional antioxidant. Their effects on the rheometric, physico-mechanical and electrical properties of NBR composites were evaluated. Thermo-oxidative aging was carried out for NBR composites and distribution of the prepared products observed by Scanning Electron Microscope (SEM).The results showed that the prepared products can act as highly efficient antioxidants in acrylonitrile butadiene rubber vulcanizates comparing with commercial antioxidant TMQ and revealed that there was enhancement in mechanical properties of NBR composites that containing the prepared products, as well. The results also illustrated that the optimum ratio from 2-alkylbenzimidazole incorporated into acrylonitrile butadiene rubber vulcanizates is 1.5 phr if compared with the same ratio from traditional antioxidant (TMQ)[1]. Unsaturated chain structure of natural rubber makes it a poor defense against thermo-oxidative aging. Synthetic antioxidants are commonly used in rubber compound recipes to prevent/retard aging of the rubber material during its service life. However, synthetic antioxidants cause some negative effects on human and environmental health; they tend to be replaced by natural alternatives. In this study, the short- and long-term antioxidant effects of henna and its basic active components, lawsone and gallic acid, have been investigated individually for natural rubber cured with semi-efficient sulfur vulcanization system. The composition of henna was determined by gas chromatography-mass spectrometry (GC-MS) analysis. Qualitative and quantitative analysis were performed using Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) to highlight structural changes on aged vulcanizates. The authors attempted to correlate the suggested aging mechanism with rheological, mechanical, and morphological properties. Results showed that both lawsone and gallic acid were impressively successful regarding their anti-oxidation activity. In addition, henna, which contains a sufficient amount of lawsone and gallic acid, has been suggested as a competitive natural alternative to the common synthetic stabilization system for natural rubber, considering its sustainable commercial abundancy[2]. Generally, in most countries, there are no strict regulations regarding tire disposal. Hence, tires end up thrown in seas and lands as well as being burnt, harming the living beings, and are therefore considered a very dangerous pollution source for the environment. Over the past few years, several researchers have worked on incorporating shredded/powdered rubber tires into cement-based material. This strategy shows a dual functionality: Economic-environmental benefits and technological functionalization of the building material. Rubber-modified cement materials show interesting engineering and architectural properties due to the physical-chemical nature of the tire rubber aggregates. However, the abovementioned performances are affected by type, size, and content of polymer particles used in the cement-based mixtures production. Whereas an increase in the rubber content in the cement mix will negatively affect the mechanical properties of the material as a decrease in its compression strength. This aspect is crucial for the use of the material in building applications, where proper structural integrity must be guaranteed. In this context, the development of innovative manufacturing technologies and the use of multi-physics simulation software represent useful approaches for the study of shapes and geometries designed to maximize the technological properties of the material. After an overview on the performances of 3D printable rubber-cement mixtures developed in our research laboratory, a preliminary experimental Finite Element Method (FEM) analysis will be described. The modeling work aims to highlight how the topology optimization allows maximizing of the physical-mechanical performances of a standard rubber-cement component for building-architectural applications[3-7]. This paper discusses the application of piezoceramic bender elements (BEs) for measurement of shear wave velocity in the time and frequency domain in a triaxial cell under different isotropic confinement. Different interpretation methods were used in the tests and their results were finally compared with each other. Two types of anthropogenic material were tested: pure Recycled Concrete Aggregate (RCA) and RCA-rubber chips mixtures (15% of rubber addition). Presented study is an attempt to describe dynamic properties, in terms of shear wave velocity (VS), of the aforementioned anthropogenic material using the technique commonly applied for natural soil. Although some research is currently being carried out, in order to evaluate physical, chemical and mechanical properties of RCA and rubber-soil mixtures, still little is known of their dynamic properties. Hence, this work will provide the experimental results of shear wave velocity of RCA and its modified version. The results show that tires chips significantly decrease the VS values of modified RCA. They help to reduce the near field effect, but the received parameters are more incoherent. The VS values were found to be influenced by interpretation technique, mean effective stress and wave's propagation period. The maximum VS values were obtained mostly from the frequency domain method, although time domain analysis gives the results that are more coherent[4]. In this paper, the ethylene propylene diene monomer (EPDM) rubber-based dough recipe for a conveyor belt used in high temperature conditions was developed. As a first step, the silica loading effect on the mechanical and

rheological properties was determined. After selecting the proper coating dough recipe, dough properties were investigated for filler mica, instead of silica, and the influence of paraffinic oil was tested for both silica and mica fillers. The properties of the EPDM rubber blend were investigated with rheometer tests on the semi-finished materials and with mechanical and physical tests (tensile strength, elongation at break, density, hardness, abrasion, heat ageing tests) on the finished coating materials after a vulcanization process. Thermal degradation behaviors of materials were analyzed by the thermal gravimetric analysis (TGA) system, and determination of chemical structure was analyzed by Fourier transform infrared spectroscopy (FTIR). The physico-mechanical characteristics of EPDM rubber blends were increased with silica loadings. EPDM rubber demonstrates thermal resistance in the temperature range of 150 o C – 160 o C under normal conditions. As a result of the studies conducted, the heat resistance of the coating rubber material was raised to 200 o C by adding silica and paraffinic oil with a higher flash point into the EPDM dough mixture formulae[5]. The resistance of biodiesel fuels to autoxidation can be improved by mixing them with antioxidants. In this study, the effectiveness of 10 conventional antioxidants added to rubber seed oil biodiesel was investigated. According to the Chinese Pharmacopoeia (2015 version), the soluble interval was evaluated and Rancimat method using EN 14112 was adopted to determine the antioxidative effect of conventional antioxidants in rubber seed oil biodiesel. Moreover, this study also revealed the oil-soluble properties of conventional antioxidants in biodiesel at different temperatures and investigated the change rule of their oil-soluble properties. The results indicated that 10 common antioxidants could improve the antioxidative performance of rubber seed oil biodiesel to a certain extent; however, their effects were quite different. At room temperature (20 °C), conventional antioxidants exhibited relatively poor oil-soluble properties, with great discrepancy. The decreasing order of oil-soluble properties of 10 conventional antioxidants in rubber seed oil biodiesel is as follows: BHA > TBHQ > D-TBHQ > PA > PG > OG > VC > MT > AP > GA. With increasing temperature, the oil-soluble properties of 10 antioxidants somewhat improved; however, their soluble interval changed only slightly. A weak relationship was observed between the antioxidative performance and oil-soluble properties of 10 conventional antioxidants. Noteworthy, in practical production applications, the antioxidative performance and oil-soluble properties of antioxidants are important factors in the selection of appropriate antioxidants [6].

Experimental part

Experimental tests of microcrystalline paraffin raw materials based on technical standards (GOST 6617-76) were conducted in the laboratories of the Tashkent Research Institute of Chemical Technology and the First Rubber Engineering Plant LLC, and the results are given in Table 1 below.

Table 1. Results of microcrystalline paraffin raw material tested in the laboratory of chemical analysis

№	Test names	Indicators		Technical method	Compliance indicators
		ГОСТ 6617-76 by request	In practice		
1	Freezing temperature, ˚C	61-69	63.2	ASTM D938	Appropriate
2	Kinematic viscosity 100 ˚C да	5.5-8.5	7.8	ASTM D445	Appropriate
3	Ash composition % ≤	0.3	0.06	ASTM D4574	Appropriate
4	Loss of mass ≤%, 125˚C да	0.3	-0.008	ISO-787-2	Appropriate

The results of the chemical analysis revealed that the raw material meets the requirements of conformity and technical requirements. After chemical analysis, 101-H and 101-L rubber compounds were prepared in the laboratory under the standard recipe for the use of microcrystalline paraffin raw material, which replaces the antioxidant SUNNOC raw material, in a small mass in the physics-mechanical test laboratory. was performed on the device. The rubber mixture from the valve is poured into a vulcanizing flat press machine at 55 gr. was removed from the rubber mixture and placed in molds and baked at 150˚C for 15 minutes at a pressure of 6-7 MPa. The mature rubber mixture from the vulcanizing flat press was cooled to room temperature for 16 h and samples were taken for testing. (Figure 1a and b).

Figure 1a.
Sample baked in press form under pressure of 6-7 MPa for 15 minutes at 150 ˚C.

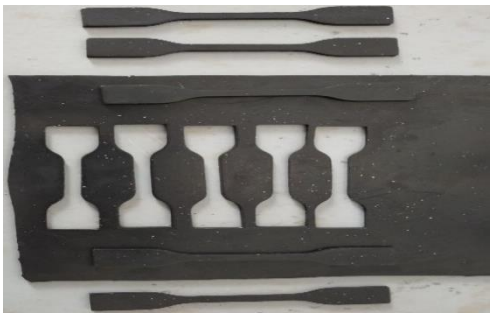


Figure 1b.
Sample for testing on the device "Electronic breakthrough machine" AI-7000 ".

Results and its discussion

In the laboratory conditions of the cooled rubber mixture on the device "Electronic rupture machine" AI-7000 "were tested such parameters as tensile strength, relative elongation at break, elasticity, modulus of elasticity; The kinetics of the vulcanization process and the hardness of the device "Measurement of solidity on Shoru N14 / 1" were studied in the device "Rotary rheometer (Vulcanization device without rotor) M-3000A" and the results are given in Table 2.

Table 2. Results of hardness, relative elongation, tensile strength and kinetics of vulcanization of rubber mixtures obtained under laboratory conditions

№	Rubber compound brand	Hardness	Delay in relative expansion	Strength in rupture ≥MPa	1800C*4min			
					The vulcanization process			
			N/mm	MPa	T10 s	T90 s	ML dNm	MH dNm
1	According to the normative documents	≤85	≥ 500	≥ 26	84	150	5.0	15
					61	116,5	3,2	11,5
					38	83	1,5	8
	101-H	64	561,66	27,09	51,41	114,61	2,38	12,71
2	According to the normative documents	≤ 85	≥440	≥17	36	75	2	10
					55	112,5	4,3	15
					74	150	6,5	20
	101-L	65	585,66	18,55	47,69	101,90	2,65	12,99

In Table 2, it can be seen that the hardness, relative expansion elongation, elongation-elongation strength and vulcanization process kinetics tests of 101-H and 101-L rubber compounds under laboratory conditions meet all technical requirements.

Results of laboratory tests of 101-N, 101-L rubber compounds obtained as a result of wear processes. Are given in Table 3.

Table 3. Results of physical and mechanical performance of rubber compounds obtained after the aging process

After the aging process					
Rubber compound brand	Loss of friction	Rigidness	Power at interruption	Delay in relative expansion	Strength in rupture
According to the normative documents	mm	≤	N	%≥	≥MPa
	≤115	64	≥	≥375	≥20
101-H	77	77	219,41	528,62	27,43

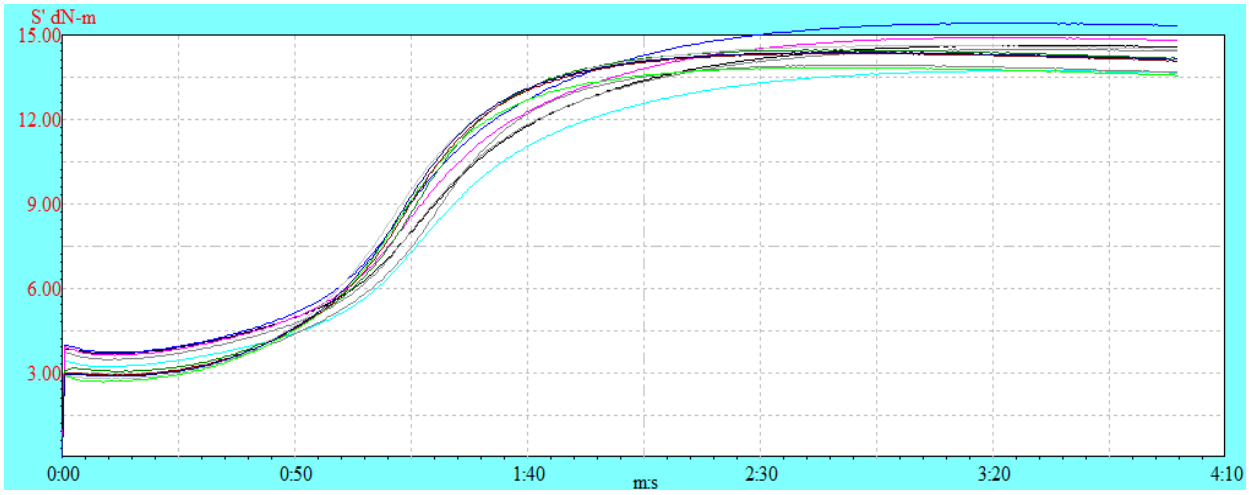
According to the normative documents	≤185	≤64	≥	≥330	≥13
101-L	120	65	149,29	475,2	18,66

Laboratory tests of 101-H and 101-L rubber compounds obtained under laboratory conditions on hardness, relative expansion elongation, elongation, elongation, strength, vulcanization process kinetics (Table 2), post-wear processes (Table 3) 101-N, 101-L rubber compounds were prepared and tested in the rubber compounding shop in the technology of production of mixtures, and the results of the obtained results are given in Table 4.

Table 4. Test results obtained in a rapid laboratory of rubber compounds used in production (technology)

№	Rubber compound brand	Hardness	Relative elongation	Strength in rupture ≥MPa	1800C*4min Volcanization kinetics			
			N/mm	MPa	T10 s	T90 s	ML dNm	MH dNm
1	According to the normative documents	≤85	≥ 500	≥ 26	84	150	5.0	15
					61	116,5	3,2	11,5
					38	83	1,5	8
	101-H	65	568,27	24,93	43,34	106,74	3,16	12,05
2	According to the normative documents	≤ 85	≥440	≥17	36	75	2	10
					55	112,5	4,3	15
					74	150	6,5	20
	101-L	65	630,94	19,4	34	102,15	3,72	14,29

In technology, the results obtained when using microcrystalline paraffin raw material instead of the antioxidant SUNNOC raw material for rubber compounds were determined in accordance with technical test standards. Graphical lines of vulcanization kinetics "Rotary rheometer (Vulcanization device without rotor) Model machine: M-3000A" was obtained and graph 1 shows the graphical lines of vulcanization kinetics.



1-graph. Location of graph lines during vulcanization.

The location of the graph lines of the vulcanization process kinetics shows that the microcrystalline paraffin did not adversely affect the vulcanization process, which can be explained by the fact that the graph lines lie in the same plane.

Conclusion: The physical and mechanical properties of the rubber mixture obtained on the basis of microcrystalline paraffin raw materials, such as vulcanization process kinetics, hardness, tensile strength, relative elongation at break, modulus of elasticity, were studied and found to meet all technical requirements and norms.

So, based on these findings, effective results were obtained when using low-cost local raw material

microcrystalline paraffin instead of antioxidant SUNNOC raw material for the production of conveyor belts at BRZ LLC.

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