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Study of the Cement Additives Effect on the Physical and Mechanical Characteristics of Rubber Material

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Abstract: *The materials of the article are devoted to obtaining the material based on a mixture of natural rubber with the refractory cement filler in a certain proportion and the study of its physical and mechanical characteristics. The samples with different cement contents were formed to determine the optimal proportion of cement additives in the mixture. The resulting analysis showed that the material with a cement proportion of 15 (pphr) has the best characteristics, in which an increase in the values of the maximum tensile pressure (8.98 MPa) was achieved, a decrease in the values of elongation, while an increase in the value of hardness and wear resistance, and minimum level of absorption was observed when the samples were immersed in technical oil - by 1.29%.*

Keywords: *rubber, cement, vulcanization, mechanical characteristics*

1.Introduction

Modified kinds of plastics are increasingly used to replace important materials such as metal, wood and glass in various industries because they have a number of advantages that are not present in the above. Such kinds of plastics are successfully used for manufacturing of hulls and other parts of production machinery, vehicles, ships and aircraft. In addition to technical plastics the rubber-based products are also widely used, which have a number of advantages, such as moisture resistance and flexibility. Moreover, it is used in those areas where the elements used must have good mechanical properties, flexibility, heat and wear resistance. In this regard, many scientists have conducted research to find fillers or polymer materials that can significantly improve some of the properties of rubber [1-4].

In particular, the researcher [5] studied the effect of adding layered silicates with a layer thickness of 1 (nm) to the rubber, thereby lowering the vulcanization temperature and increasing the chemical bond between its components. Another researcher [6] investigated the effect of adding different proportions of clay on the properties of the rubber polymer. Samples of nanocomposites based on rubber polymer with clay with different proportion were obtained, which were subjected to further studies.

A team of scientists [7] studied the effect of cement additives on the properties of nitrile rubber. In the study, rubber compounds were prepared that have the ability to withstand atmospheric conditions for their further use as shock dampeners. The results showed that after adding 50% cement, the hardness increased by 64%, the viscosity by 155%, the tensile strength by 218%, and the modulus of elasticity by 235%. At the same time, the relative elongation was reduced by 90%, the specific gravity by 42%. Thus, it was proved that the addition of 50% cement to nitrile rubber resulted in a positive improvement in the overall properties of rubber.

The researchers [8] added appropriate amounts of borax powder (5, 10, 15, and 20 pphr) to various rubbers to study the effect of borax addition on the vulcanization properties of rubber: styrene-butadiene rubber (SBR), nitrile rubber (NBR) and polychloroprene rubber (WRT), as well as to study the properties of viscosity, flexibility (curing time) and plasticity variation (scorch time). The results showed that the addition of borax to SBR reduced the viscosity of rubber products, had a significant effect on mechanical properties and made them more plastic. In contrast, when borax was added to NBR, viscosity increased slightly but steadily, and viscosity increased to 10 (pphr) when added to RB, which increased the mechanical properties of rubber.

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The researchers [9] studied the effect of adding shell powder with different proportion (20, 30, 50, 100, 120 and 150 pphr) on the mechanical properties of natural rubber at a concentration of calcium carbonate $CaCO_3$ 82.4%, noting the degree of this effect on the mechanical properties of rubber, which included both hardness and tensile strength. The obtained results showed an increase in the hardness of rubber with an increase in the percentage of shell powder. It was also noted that with the addition of 20 (pphr) shell powder, the value of the tensile strength of rubber increased, but with an increase in this percentage it significantly decreased due to an increase in its hardness.

The researcher [10] added kaolin and vegetable oil as a plasticizer in the mixture of natural rubber with butadiene nitrile rubber, ethylene rubber and propylenediene monomer.

The results showed that the mechanical properties of composite rubber are influenced by the proportions of each of the natural rubbers, kaolin and technical oils used as plasticizers, as well as the degree of crosslinking between the particles of the material.

The researcher [11] authors conducted the experiments to assess the effects of temperature on the compressive strength, splitting tensile strength and flexural strength of rubberized concrete. The results indicate that the addition of rubber particles can enhance the resistance of concrete to high temperatures. The study also found that the optimal rubber content in the concrete mixture depends on the desired mechanical properties and temperature conditions. These findings have implications for the design and construction of fire-resistant structures and can contribute to the development of more durable and reliable concrete materials.

The researcher [12] authors conducted the experiments with the different ratios of components to determine the optimal conditions for achieving desired concrete properties. Parameters such as strength, elasticity and density of the concrete were investigated. The research findings show that the addition of rubber powder and silica fume can significantly improve the strength and elasticity of the concrete. Additionally, certain ratios of these components were found to enhance the heat resistance of the concrete.

The researcher [13] authors conducted the experiments with the different ratios of these components to determine the optimal conditions for achieving desired concrete properties. Parameters such as strength, elasticity, and density of the concrete were studied. The research findings indicate that the addition of rubber powder and silica fume can significantly enhance the strength and elasticity of concrete. Furthermore, specific ratios of these components were found to improve the heat resistance of concrete.

The objective of the the study of the refractory cement additives effect in various proportions as a filler on the properties of the natural rubber to obtain mixtures with the best properties.

2. Methods and materials

2.1. Practical section

The samples of natural rubber STR 20 made in Iran were prepared in these studies. Table 1 shows the main characteristics of additives and manufacturing companies.

Table 1. Materials included in the composition of the rubber mixture

№	Material	Properties	Value	Company
1	Carbon Black	1-SP. gravity (typical)	1.8	Aditya Birla Group. India
		2-iodine absorption	36 ± 5 mg/g	
		3-Ash content	0.75%	
2	Zinc oxide	1-SP. gravity (typical)	5.5	Arabian zinc oxide factory. kSA
		2-zinc oxide content	99 min	
3	Stearic acid	1-SP. gravity (typical)	0.85	Zhengzhou Sino Chemical Co. Chine
		2-iodine value	8g12/100g	
		3- acid value	195-213	
		4-Ash at 550ºC	0.1%	
4	sulfur	1-SP. gravity (typical)	1.57	Universal Chemicals. co-India
		2- sulfure content	80 ± 2%	
		3-Ash at 550ºC	0.2% max	

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5	Antioxidant TMQ	1-SP. gravity	1.08	Sunchemy
		2-Healting loss, ≤	0.3%	International. Co.Ltd- Chine
		3-Ash at 550ºC	0.3%	
6	Process oil	1-sp. gravity 2-Viscosity at 0ºC 3-Ash at 55ºC ≤	0.89 480 secs 0.01%	Grandocean Enterprise Group Co., Ltd- Chine
7	Thiuram	1- Thiuram content 2-Ash content % ≤	98 min 0.3	Rongcheng Chemical General Factory Co. Ltd- Chine

To determine the effect of fireproof cement on mechanical and chemical properties of rubber, cement was added by a multi-proportion with 40% aluminum oxide Al_2O_3, 40% silicone oxide SiO_2 and 20% calcium carbonate $CaCO_3$ while using:

1 - a rolling machine for mixing rubber and a mixture weighing 1 kg as shown in Figure 2 with two metal rolls with length 340 mm and diameter 180 mm covered with the layer of high strength chromium between which there is a controlled rotation distance in opposite directions to each other, with different speeds: two front rolls have a speed of 27.5 (rpm) and back - 22 (rpm) [14].

2 - A mold for forming rubber sheets.

3 - Tensile testing device.

4 - A device for measuring frictional resistance.

5 - A device for measuring hardness.

6 - The accurate electronic scales of the «Kem» type with an accuracy of 0.0001 G.

7 - A glass tube with a capacity of 25 mL for measuring the density of rubber, determining the weight on the accurate scales.

8 - Hydraulic press with electric heater, in which the temperature can be raised to 250°C, equipped with a cooling system.

2.2. Experimenting and testing

The preparation of the rubber mixture was conducted using a rolling machine (Figure 1), the mixing operation was conducted in accordance with the ASTM D15 standard [15], which established: operating temperature regimes, the sequence of loading materials into the machine, the period of homogenization time, ensuring the production of samples homogeneous in composition and thickness with the content of various proportions of refractory cement (0, 5, 10, 15, 20 (pphr)).

The laboratory samples are created by applying them using a laboratory piston with dimensions of 16 x 20 cm, operating at a hydraulic pressure of 30 bar, regulated by a pressure gauge installed in the control unit, and in rotating cylinders there is oil heated to a temperature of 90°C, regulated by a thermometer located in the same unit. The heating process and pressure mode are maintained for 10 min, after which the samples were cooled with the water under the constant pressure at the temperature of 40°C [10] and left for 24 h before the start of testing.

Figure 1. The rolling machine for forming samples

2.3. Forming of rubber samples

The process of forming rubber samples was conducted due to the following algorithm:

1. Table 2 shows the percentage of materials included in all prepared rubber mixtures. To obtain samples from natural rubber, the kneading process is carried out before adding accompanying materials to them using rolls. The preparation of the rubber mixture, which is the basis for the manufacture of samples, is conducted by repeatedly passing it between gradually converging rolls for 3-4 min until uniformity is obtained while keeping the temperature regime.

Table 2. Percentage of materials included in the rubber mixture

	Pphr
Rubber STR 20	100
Stearic acid	2
Zinc oxide	5
Process oil	2
Carbon Black	10
Cement	0/5/10/15/20
Antioxidant (TMQ)	1
Thiuram	1
Sulfur	5

2. Stearic acid was added to the mixture and kneaded for a minute until homogeneity was obtained.
3. Zinc oxide was added and kneaded well until a homogeneous mass was obtained.
4. Then mineral oil was added and kneaded until smooth.
5. The first part of carbon and cement were added and kneaded until homogeneous.
6. Next, an antioxidant (TMQ) and accelerators were added and kneaded until homogeneous.
7. The second part of carbon and cement were added and kneaded until homogeneous.
8. Then sulfate was added as a rubber vulcanizer, which leads to the creation of a lattice structure that increases its hardness and stability. After that, the mixture on the rollers was turned over for a while until the sulfate was distributed in all parts of the rubber mixture equally and homogeneously, and then it was pulled in thickness.
9. Next, the mixture was cooled to room temperature, as shown in Figure 2, while the operating time on the rolling machine was 20 - 25 min.

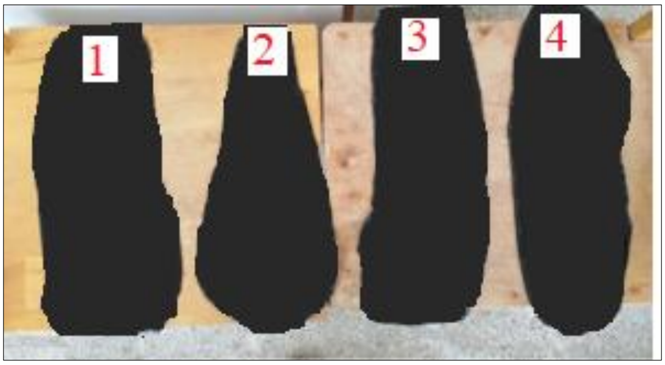

Figure 2. The molded rubber samples

10. After the end of the kneading process the resulting mixture was vulcanized by placing it in a rectangular shape (20x16 cm), and then to complete the molding process it was placed in a hydraulic press at the pressure of 30 bar and at the temperature of 90°C, and this process took 10 min.
11. Next, the samples were cooled through a cooling loop located inside the piston containing inlet and outlet openings for water. The pressure was controlled and kept constantly throughout the cooling

process. Cooling continued until the temperature reached 40°C, at which the sample took a fixed shape [16].

12. The cooling process was stopped and the pressure was removed, and then the samples were removed from the mold, as shown in Figure 3, and left for 24 h before the start of testing.

Figure 3. The finished samples

2.4. Tensile test

This test was conducted in accordance with ASTM D-412 using the stretching device shown in Figure 4.

Figure 4. The tensile testing device

Figure 5 shows one of the prepared tensile test samples.

Figure 5. The tensile test sample

2.5. Hardness test

This test was conducted in accordance with DIN-53505 using a digital Shore hardness tester shown in Figure 6. The test samples were squares with dimensions of 40 x 40 mm and a thickness of 6 mm, as shown in Figure 8.

Figure 6. The hardness tester

Figure 7. The samples for determination of hardness

2.6. Swelling test

This test was conducted in accordance with the ASTM-D471 standard by immersing prepared samples with dimensions (30 x 30 x 6 mm) in various solvents (diesel fuel, gasoline and technical oil), as shown in Figure 8, while the samples were weighed every three hours for 24 h, and the efficiency was calculated according to the following dependence:

$$SR = (W_2 - W_1 / W_1) \cdot 100,$$

where:

SR - the efficiency, (%);

W_1 - the sample weight before immersing, (g);

W_2 - the sample weight after immersing, (g).

Figure 8. The solvent testing of samples
(1- gasoline, 2- diesel fuel, 3- technical oil)

2.7. Friction resistance test

The friction resistance test was conducted in accordance with DIN-53516 by calculating the weight loss using the rubber abrasion resistance testing machine shown in Figure 9, in which the wear value was calculated as a function of the degree of abrasion of the sandpaper, the value of which was similar to that taken from ISO 1891 (Part 1), then the volume of wear (*V*) was calculated by the ratio:

$$V = \frac{\Delta m \cdot S}{\rho},$$

where:

V - the volume of wear, mm^3;

$\Delta m = m_1 - m_2$ - the weight of removed material, mg;

m_1 - the weight of the sample before the experiment, mg;

m_2 - the weight of the sample after the experiment, mg;

S = 200 (mg) – the wear constant calculated according to the standard friction path;

ρ - the sample density, mg/mm^3.

Figure 9. The friction measuring device

Figure 10. The electronic scales with high sensitivity

3. Results and discussions

3.1. Study of mechanical and physical properties

3.1.1. Tensile strength

Figure 11 presents the test results, which show the effect of adding various proportion of refractory cement to the material of the samples under study on the values of the tensile strength. Analyzing the results, it can be noted that a change in the tensile stress depending on the cement proportion, the values of which for STR20 type rubber increased with increasing cement proportion, reaching its maximum value of 8.9 (MPa) with the addition of 15 (pphr), and then, with further increase, it begins to decrease.

An increase to the value of 15 (pphr) is associated with an increase in the physico-chemical bond and an increase in the bonding force between the components of the cement material with rubber chains. This can be explained by the formation of bonds between free radicals formed on rubber chains and between empty orbitals in cement oxides, which leads to an increase in tensile strength. These results are coordinated with the results of studies [17,18]. An increase in the additive above 15 (pphr) reduces the tensile strength, since the oxides in the cement material playing the role of filler fills the voids between the chains without binding them together.

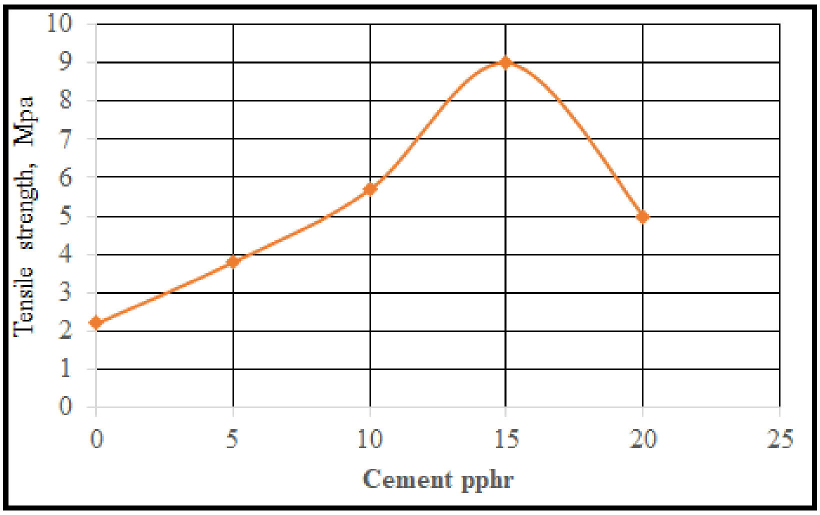

Figure 11. The effect of the proportion of refractory cement at tensile strength

3.1.2. Properties of elongation at break

Under these experiments the effect of the proportion of refractory cement additives in prepared rubber samples on the magnitude of their elongation was studied. Figure 12 shows a gradual and continuous decrease in the elongation value with an increase in the proportion of cement, the granules of which act as fixators of the structure [18], hindering the freedom of movement of macro chains, as well as increasing the relationship with the chains of neighboring macromolecules, which limits their freedom of movement and prevents the process of reorientation of chains causing elongation.

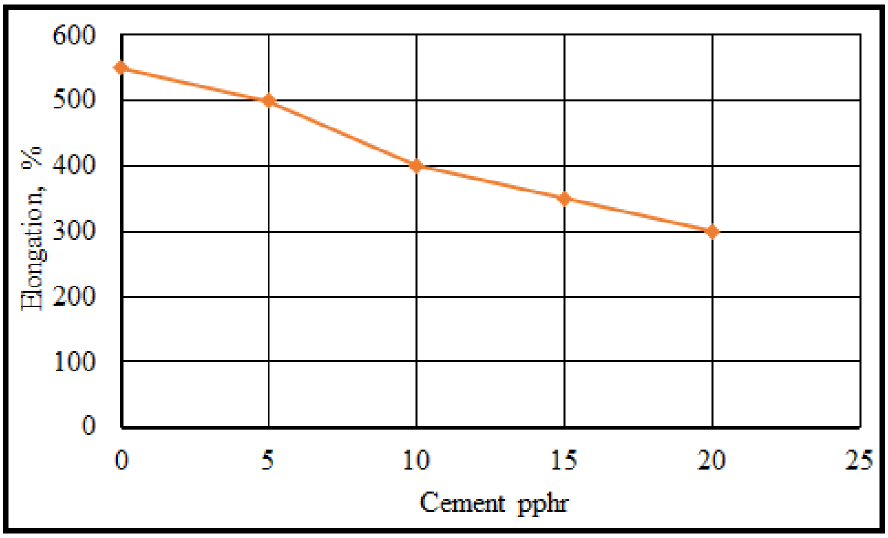

Figure 12. The effect of the proportion of refractory cement on elongation

3.1.3. Hardness properties

Figure 13 shows the relationship between the proportion of refractory cement additives and the hardness of rubber samples, and it can be noticed that when adding a percentage of cement 5 pphr, the hardness of Shore A increased from 40 units to 53 units, and when 10 pphr it increased to 55 units, and when 15 pphr - up to 56.5.This is due to an increase in the physical bond and cohesion of the filler with rubber [17]. The relationship between the hardness and the portion content of the additive, which increases with an increase in these proportions, is direct, since hardening works to increase the physical bond.

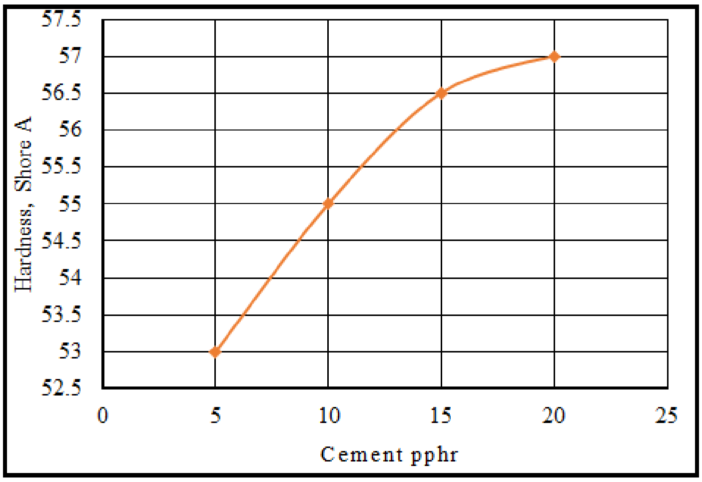

Figure 13. The effect of the proportion of refractory cement on hardness

3.1.4. Friction resistance

Figure 14 shows the results of testing the prepared samples for friction resistance. It can be seen from the figure that the decrease in the volume of wear occurs to the value180 mm^3 with of the additive proportion 5 pphr, and at 10 pphr - up to 150 mm^3, and at 15 pphr - up to 100 mm^3 15 (pphr), which is due to the homogeneity of the granulometric composition of cement and the absence of large particles, since their loss, with resistance to friction, causes an increase in the mass loss of rubber [19]. In addition, the adhesion of filler particles to rubber increases. It is also possible to notice an increase in the volume of wear after this value due to an increase in the hardness of rubber and the presence of structural defects arising from filling natural rubber with unreacted cement.

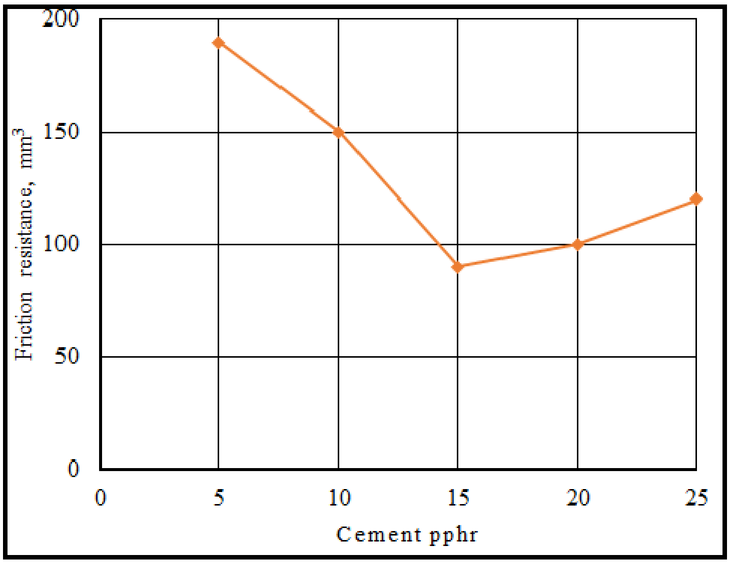

Figure 14. The effect of the proportion of refractory cement on friction resistance

3.2. Chemical properties

3.2.1. Degree of absorption (%)

These experiments were devoted to studying the degree of absorption of the prepared samples when placed in three different environments: technical oil, diesel fuel and gasoline, the results of which are shown in Figure 15. After analyzing the results obtained, it can be noted that with an increase in the percentage of cement, the degree of absorption decreased, since the ingress of cement particles into the voids between the rubber chains causes a decrease in the free volume, which limits the possibility of solvent particles penetrating into these voids, despite their small size [19]. In this regard, the filler is a material that repels non-polar organic solvents, that is, it does not absorb, therefore its presence in the structure of rubber reduces the absorption of solvents by rubber. In addition, these oxides contribute to the crosslinking of the rubber structure, contributing to the percentage of formation of strong bonds, and the structure obtained in this way will be more cohesive. Thus, the intermediate result is the prevention of penetration of organic solvent molecules, and the final result is a decrease in the rate of absorption into the rubber mixture.

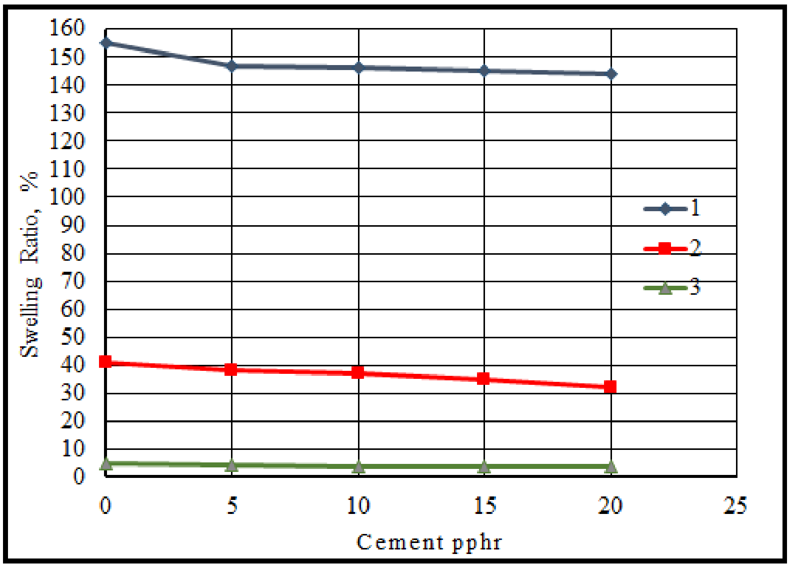

Figure 15. The effect of adding the proportion of refractory cement on the percentage of absorption of samples when they are immersed in various solvents

4. Conclusions

After analyzing the results obtained, the following can be concluded:

- the addition of refractory cement in a proportion of 15 (pphr) to natural rubber had a positive effect on its physico-mechanical properties, in which the tensile stresses values increased to a maximum value of 8.98 (MPa) with a gradual and continuous decrease in the values of elongation, while the hardness value of natural rubber increased, and the volume of wear, with an increase in the proportion of cement additives, decreased;

-when immersed in gasoline, the absorption of natural rubber samples decreased by 14.15%, in diesel fuel - by 12.43%, and the lowest degree of absorption was observed when they were immersed in technical oil - by 1.29%.

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