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RESEARCH ARTICLE

Surface treatments of nitrile butadiene rubber to enhance wear resistance and mechanical properties

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Abstract

Objectives. The aim of this work is to investigate rapid surface treatment methods of nitrile butadiene rubber (NBR) using an elastomer composition based on fluoropolymer FKM-32 and fluoroplastic F32L. The article presents new methods for enhancing the mechanical and wear properties of NBR by applying surface coatings.

Methods. Abrasion tests were conducted using an MI-2 tribometer; determination of the tensile strength properties of the samples was performed using a DVT GP UG 5 universal testing machine (*Devotrans*, Turkey). Hardness was ascertained using a Shore A type durometer. Samples were cut out on a pneumatic punching press GT-7016-AR (*GOTECH Testing Machines Inc*., Istanbul, Turkey). Microstructure and elemental composition studies were carried out using a Vega 3 scanning electron microscope (*TESCAN*, Brno, Czech Republic) equipped with an X-Act (*Oxford Instruments*, High Wycombe, United Kingdom) energy-dispersive analysis attachment.

Results. The immersion of NBR in a 10% solution of poly(vinylidene fluoride-co-chlorotrifluoroethylene) (fluoroplast F32L) in 1,1,2-trifluoro-1,2,2-trichloroethane was found to result in the formation of a uniform fluoropolymer-based coating on the rubber surface. This coating results in a decrease in the abrasion value from 0.046 to 0.005 m^3/TJ, corresponding to an increase in abrasion resistance. Furthermore, for rubbers coated by immersion in the fluoroplastic solution, the modulus at 100% and 300% strain increases by 86% and 44%, respectively, while the tensile strength increases by 20%, and the hardness increases by 9 units compared to the as-obtained NBR.

Conclusions. Regardless of pre-soaking in methyl ethyl ketone, the wear resistance of the synthetic rubber is not increased by surface treatment with elastomeric composition based on fluororubber FKM-32 grade followed by thermostating. However, surface-modification of NBR using the M3 method demonstrates better tribological performance and mechanical performance than the untreated sample. A complex of enhanced properties of surface-modified NBR-M3 can be effected by the presence of halogen atoms on the surface layer of the rubber sample.

Keywords

nitrile-butadiene rubber, fluoropolymer, fluoroplastic, wear resistance, mechanical properties

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НАУЧНАЯ СТАТЬЯ

Обработка поверхности бутадиен-нитрильного каучука для повышения износостойкости и механических свойств

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Аннотация

Цели. Разработать новые методы повышения механических и износостойких свойств бутадиен-нитрильных каучуков (nitrile butadiene rubber, NBR) путем нанесения поверхностных покрытий и исследовать методы быстрой обработки поверхности NBR с использованием эластомерной композиции на основе фторполимера ФКМ-32 и фторопласта F32L.

Методы. Испытания на истирание проводили с помощью трибометра МИ-2, определение прочностных свойств образцов — с помощью универсальной испытательной машины DVT GP UG 5 (*Devotrans*, Турция), твердость — с помощью твердомера типа Шор А. Образцы были вырезаны на пневматическом штамповочном прессе GT-7016-AR (*GOTECH Testing Machines Inc.*, Стамбул, Турция). Исследование микроструктуры и элементного состава проводили с помощью сканирующего электронного микроскопа Vega 3 (*TESCAN*, Брно, Чехия), оснащенного энергодисперсионной аналитической приставкой X-Act (*Oxford Instruments*, Хай-Вайкомб, Великобритания).

Результаты. Установлено, что погружение NBR в 10%-ный раствор поливинилиденфторида-трифторхлорэтилена (фторопласта F32L) в 1,1,2-трифтор-1,2,2-трихлорэтане приводит к образованию на поверхности резины равномерного покрытия на основе фторполимера и вызывает снижение величины абразивного износа (истираемость) с 0.046 до 0.005 м^3/ТДж, что соответствует существенному повышению абразивной стойкости NBR. Для каучуков, покрытых погружением во фторопластовый раствор, модуль упругости при 100 и 300%-ных деформациях увеличивается на 86 и 44% соответственно, в то время как прочность на растяжение увеличивается на 20%, а твердость увеличивается на 9 единиц по сравнению с полученным NBR.

Выводы. Обработка поверхности NBR эластомерным составом на основе фторкаучука марки ФКМ-32 с последующим термостатированием не позволяет снизить износостойкость резины независимо от предварительного замачивания в метилэтилкетоне. Модифицированный по поверхности NBR (методом М3) показывает лучшие трибологические и механические характеристики, чем необработанный образец. Наличие атомов галогенов на поверхностном слое образца отвечает за комплекс повышенных свойств поверхностно-модифицированного NBR-М3.

Ключевые слова

бутадиен-нитрильный каучук, фторполимер, фторопласт, износостойкость, механические свойства

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INTRODUCTION

In order to achieve the desired surface characteristics of rubber materials, various techniques have been developed. Of particular importance is surface modification, which can significantly change the material's friction characteristics, permeability, thermal stability, and mechanical properties. Methods used for surface modification purposes include those aimed at improving wear resistance and mechanical properties of rubber materials. These include surface irradiation [1], laser manipulation [2], corona discharge [3], plasma treatment including [4], photochemical modifications [5], and surface etching with an oxidation solution such as concentrated sulfuric acid and zirconium phosphate [6–8], as well as magnetron-sputtering [9, 10]. However, the mentioned technologies are typically complex and expensive. Therefore, the aim of the present work is to explore a cost-effective and efficient approach to improving the tribological characteristics of rubber materials.

Surface halogenation effects are achieved on vulcanized rubber through chemical treatment using free halogen in organic solutions or the gaseous phase, and/or inorganic and organic halogenating agents. The foundation for priority research on polymer halogenation processes, including chlorination and fluorination of rubber surfaces, was established by studies conducted as far back as the 1960s. Significant contributions to the development of halogen-based modification of elastomers were made by researchers such as A.A. Dontsov [11], V.S. Yurovsky [12], Z.N. Nudelman [13–15], I.A. Tutorsky [16], and others. One method described involves chlorinating the surface of SBR using an organic liquid (1,3,5-trichloro-1,3,5-triazinane-2,4,6-trione, TCICA) in ethyl acetate [17]. Surface modification methods of rubber with halogen-containing compounds also include surface treatment using aqueous chlorinating agents, such as HCl-acidified sodium hypochlorite solution in both aqueous and ethanol solutions [18], and organic chlorine salt (sodium dichloro-isocyanurate) [19]. Here, poly(vinylidene fluoride-co-chlorotrifluoroethylene) (PVDF-CTFE) powder was used as a friction-modifying additive for rubber matrices. The study [20] describes a developed approach to obtaining neoprene- and silicone-based elastomers with a low coefficient of friction. The described rubbers were characterized by low physical and frictional properties due to poor compatibility of PVDF-CTFE powder. Recycled poly(vinylidene fluoride-co-chlorotrifluoroethylene) (r-PVDF-CTFE) was employed to prepare nitrile rubber (NBR)/r-PVDF-CTFE composites, characterized by increase in modulus at 300% and 27.8% and decrease in swelling index. Direct fluorination by F_2 has been employed to fluorinate a broad range of polymer materials, improving the hydrophilicity, surface tension, friction coefficient, and scratch resistance of rubber materials by attaching fluorine elements onto the rubber surface, forming $–CF$, $–CF_2$, or $–CF_3$ groups [21–26]. Direct fluorination can also lead to an increase in the crosslinking density of the fluoroelastomer film on the rubber surface. By increasing the contact angle it is possible to reduce wettability and surface tension while improving chemical resistance and adhesive properties of polymers. Direct fluorination can also be used to reduce the wear properties of rubbers over the course of repeated abrasion [27]. However, one of the main disadvantages of these methods is the high aggressiveness of the halogenation reagent, high labor input, undesirable presence of toxic byproducts, and complex technical design of the production process.

The present work sets out to enhance the wear resistance of synthetic rubber through surface modification with a fluoropolymer-containing solution treatment. The developed technology is characterized by a reduction in production stages through the treatment of the rubber surface with a fluorine-containing compound, as well as the exclusion of aggressive fluorine-containing modifiers from the formulation.

MATERIALS AND METHODS

Materials. NBR (BNKS-18 grade, *KZSK*, Krasnoyarsk, Russia) was used as a basic raw material. Synthetic butadiene-nitrile rubber is a copolymer of acrylic acid nitrile (17–20%) and 1,3-butadiene produced by emulsion polymerization at a temperature of 32°C. The main NBR characteristics and those of the rubber formulated based on NBR are presented in Tables 1 and 2.

Table 1. Properties of BNKS-18

Parameter	Value
Appearance	From light-yellow to dark-brown color
Mooney viscosity	40–70
Mass fraction of acrylonitrile, %	17–20
Glass transition temperature (T_g), °C	–47 ... –50
Density, kg/m³	943

Table 2. Formulation of studied samples in parts per hundred (phr) of rubber

Materials	Compound, phr
Nitrile butadiene rubber (BNKS-18)	100
Zink oxide	3
Sulfur	1.50
Stearic acid	1
Carbon black (P-324)	40
N-tert-butyl-benzothiazole sulfonamide	0.70
Total	146.20

The rubber mixes were prepared according to ASTM D 3184[1] using a two-roll mill at a temperature of 50°C. The vulcanization of rubber blends was conducted

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[1] ASTM D 3184. Standard Test Methods for Rubber-Evaluation of NR (Natural Rubber) (Reapproved 2001).

at 170°C for 15 min. Table 2 sets out the parameters of the formulation used.

Fluoropolymer (FKM-32 grade, *HaloPolymer*, Kirovo-Chepetsk, Russia) is a copolymer of vinylidene fluoride and chlorotrifluoroethylene. Fluoroelastomers such as FKM-32 are distinguished by their ability to co-vulcanize with NBR due to the presence of active functional groups in their structure. This enables the formation of an integrated coating layer that is chemically and physically bonded to the rubber substrate, resulting in a unified material with enhanced surface mechanical properties. Unlike rigid polymer coatings, FKM-32 is characterized by significant elasticity. This elasticity allows the protective layer to maintain its integrity under repeated bending, stretching, and other mechanical stresses. FKM-32 is compatible with specific vulcanizing agents, such as *p*-quinone dioxime derivatives, which create crosslinks within the coating that not only enhance its mechanical strength, but also promote the formation of strong adhesive bonds with the rubber surface, improving the coating's resistance to delamination and mechanical damage. The main properties of the fluoropolymer are as presented in Table 3.

Table 3. Properties of FKM-32

Parameter	Value
Appearance	White crumb with individual semitransparent particles of the product
Mooney viscosity MB (4–4) 160°C	70–95
Thermal stability (mass loss at 270°C), wt %, no more than	0.15
T_g, °C	–17
F content, wt %	54–55
Cl content, wt %	14–16

This polymer was used in combination with the vulcanizing agent (quinol ester of *p*-quinone dioxime) and the dithiophosphate accelerator for application onto the surface of NBR rubber. The quinol ester of *p*-quinone dioxime (trade name EH-1 *Minkar*, Russia) appears in the form of a powder having a light-yellow to dark-yellow color. The *p*-quinone dioxime derivative was used as a curing agent for fluoroelastomers (FKM) due to its effective promotion of the formation of a crosslinked structure, which enhances the adhesion of the coating to the substrate and improves its mechanical strength. EH-1 acts not only as a vulcanizing agent but also as an adhesion promoter for the coating to NBR, owing to its chemical reactivity and ability to form strong bonds with the substrate surface. The dithiophosphate accelerator (trade name Kvalaks C1, *NPP Kvalitet*, Moscow, Russia) is a transparent liquid ranging from yellow to brown in color with a zinc mass fraction of 8.8% and a kinematic viscosity at 100°C of not less than 6 cSt. The final formulation of the composition based on fluoropolymer is presented in Table 4. Quinol ether was chosen as the vulcanizing agent, which is capable of structuring halogen-containing—in our case, fluorine-containing—rubbers. Accelerator and the vulcanizing agent dissolve well in methyl ethyl ketone (MEK).

Table 4. Formulation of the composition based on fluoropolymer (FKM-32)

Materials	Compound, phr
Fluoropolymer (FKM-32)	100
Dithiophosphate accelerator	2
The quinol ester of *p*-quinone dioxime	6

The elastomeric composition of this formulation (Table 4) is prepared as a 10% solution in methyl ethyl ketone. Rubbers based on NBR have a high ability to swell in MEK, which in turn facilitates the penetration of fluoropolymer into the rubber sample structure for the purpose of creating a surface-modified layer of NBR rubber.

Poly(vinylidene fluoride-co-chlorotrifluoroethylene) (fluoroplast grade F32L, *HaloPolymer*, Kirovo-Chepetsk, Russia), representing a copolymer of trifluorochloroethylene and vinylidene fluoride, is a chemically resistant polymer that dissolves well in ketones, complex esters, Freon-113, and tetrahydrofuran. Fluoroplasts, including grade F-32L, are characterized by an extremely low coefficient of friction against steel, which allows for a significant reduction in the surface friction of rubber coated with such materials. As a result, the wear resistance and durability of rubber products operating under conditions of friction, sliding, and abrasive stress are greatly improved. The copolymer based on vinylidene fluoride and chlorotrifluoroethylene exhibits excellent chemical resistance to aggressive environments, oils, solvents, and chemical agents. This material may be applied as a surface coating to create a protective barrier that prevents the penetration of aggressive substances into the rubber bulk, thereby preserving its original performance characteristics. Fluoroplast F-32L also features relatively high hardness, resulting in the formation of a rigid and wear-resistant surface layer on the rubber. This protects the softer NBR substrate from damage during contact with hard abrasive surfaces, preserving its mechanical properties and extending the service life of the product. Being soluble in a number of organic solvents (e.g., 1,1,2-trifluoro-1,2,2-trichloroethane), fluoroplast F-32L can penetrate into the rubber surface during application due to partial swelling of the elastomer. After solvent evaporation, a uniform, thin, and mechanically strong coating is formed, which is firmly bonded to the substrate at the molecular level, thus ensuring high resistance to delamination and mechanical stress. The main properties of the fluoropolymer are as presented in Table 5.

Table 5. Properties of fluoroplast F-32L

Parameter	Value
Appearance	Coarse-grained powder of white or slightly yellowish color
Density, kg/m^3	1920–1950
Thermal stability (mass loss at 270°C 5h), wt %, no more than	0.1–1.0
T_g, °C	30
Coefficient of friction on steel	0.04
Brinell hardness, MPa	29–39

As a solvent for the fluoroplastic, 1,1,2-trifluoro-1,2,2-trichloroethane (CFC-113) was used. This compound is highly volatile and is classified as a low hazard (hazard class 4), meaning it does not necessitate specific protective measures for personnel due to its low toxicity. These attributes make it suitable for this application.

Modification. Various approaches have been proposed for improving the surface properties of NBR-based rubbers through the application of functional coatings. In the present study, samples of NBR rubber were prepared as dumbbell-shaped specimens (for tensile testing) and square-shaped specimens (for abrasion tests) were subjected to different types of surface treatments. The specific surface treatment methods applied to the rubber samples are summarized in Table 6. According to these methods, the developed compositions are intended to form a uniform coating on the rubber surface, which creates a stable surface layer after drying and thermal exposure. This coating is likely to reduce wear rates and the friction coefficient by reinforcing the surface without altering the bulk structure of the vulcanizate.

Table 6. Specific surface treatment methods

Modification type	Description of the modification method
M1	An elastomer composition of the following content: FKM-32, quinol ester of *p*-quinone dioxime and dithiophosphate accelerator (10 wt % solution in MEK) were applied to the rubber surface using a brush ($T = 25 \pm 0.5$°C). The total number of applied layers was 4, with 24 h of drying time between layers. The sample with the dried coating was thermostated at a temperature of 150°C for 10 min.
M2	Pretreatment of NBR rubber was conducted by immersing in MEK for 10 min. An elastomer composition of the following content: FKM-32, quinol ester of *p*-quinone dioxime and dithiophosphate accelerator (10 wt % solution in MEK) were applied to the rubber surface using a brush ($T = 25 \pm 0.5$°C). The total number of applied layers was 4, with 24 h of drying time between layers. The sample with the dried coating was thermostated at a temperature of 150°C for 10 min.
M3	Samples of NBR were immersed in a 10% solution of fluoroplast F32L in 1,1,2-trifluoro1,2,2-trichloroethane and kept for 6 h ($T = 25 \pm 0.5$°C), after which they were dried to a constant weight.

Experimental methods. The abrasion tests were conducted using an MI-2 tribometer, designed for assessing rubber wear, according to the method for determining abrasion resistance under sliding against rigidly fixed abrasive particles according to GOST 426-77[2]. The abrasion resistance was calculated under a load of 26 N and a disk sliding rate of 40.0 rpm, with the test samples securely fixed in a holder. An abrasion disc made of stainless steel grade 25 (SS) and chrome nickel steel (CrNi) served as the abrasion surface. Volume abrasion was assessed every five minutes by weighing the samples and calculating the subsequent mass loss. The samples for the wear resistance test, with a wearing surface in the form of a square (each side measuring 20 mm), were equipped with tabs of 4 mm width and 3 mm height for attachment to the holder frame. Based on the experimental data, the following indicators were calculated.

The volume loss of the rubber (ΔV) in cm for the two tested samples is calculated using Eq. (1):

$$\Delta V = \frac{m_1 - m_2}{\rho}, \tag{1}$$

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[2] GOST 426-77. Interstate Standard. Rubber. Method for determination of abrasion resistance under slipping. Moscow: IPK Izdatelstvo standartov; 1977.

where m_1 is the mass of the two samples before the test in kg, m_2 is the mass of the two samples after the test in kg; ρ is the density of the rubber in kg/m^3.

The abrasion resistance (α) in cm^3/kW·h is calculated using Eq. (2):

$$\alpha = \frac{\Delta V}{A} \times \frac{1}{K}. \tag{2}$$

The formula for converting abrasion values from cm^3/kW·h to m^3/TJ is as follows:

$$\text{Abrasion (m}^3\text{/TJ)} = \\ = [\text{Abrasion (cm}^3\text{/kW·h)} \cdot 10^{-6}]/(3.6 \cdot 10^{-3}), \tag{3}$$

where 1 cm^3 = 10^{-6} m^3, 1 kW·h = $3.6 \cdot 10^6$ J = = $3.6 \cdot 10^{-3}$ TJ.

Abrasion resistance was calculated as loss in weight after 200 and 3000 abrasion cycles.

Determination of the tensile strength properties of the samples was performed using a DVT GP UG 5 universal testing machine (*Devotrans*, Turkey) in accordance with the ISO 37:2024 Standard[3], at a testing rate of 100 mm/min. Samples were cut out on a pneumatic punching press GT-7016-AR (*GOTECH Testing Machines Inc.*, Istanbul, Turkey). Each data point was corroborated with five measurements. Hardness was ascertained using a Shore A type durometer, adhering to the testing method outlined in the ASTM D2240-2015 (R 2021) Standard[4]. Shore hardness tests were carried out on specimens with a thickness of 6 mm.

The study of the microstructure and elemental composition of modified NBR rubber was carried out using a Vega 3 scanning electron microscope (*TESCAN*, Brno, Czech Republic) equipped with an X-Act (*Oxford Instruments*, High Wycombe, United Kingdom) energy-dispersive analysis attachment.

RESULTS AND DISCUSSION

The abrasion test was employed to evaluate changes in abrasion resistance and the average friction coefficient of both the as-received and surface-treated NBR samples (Table 7).

Analysis of the performance of samples modified using methods M1 and M2 confirms that their abrasion resistance and friction behavior remains comparable to those of the unmodified (as-received) rubber. Pretreatment involving soaking in MEK had a negligible effect on the efficiency of surface treatment.

When chrome-plated steel was used as the counterbody material, a decrease in wear resistance was observed along with an increase in the friction coefficient, indicating less favorable tribological performance. The limited effectiveness of the M1 and M2 methods may be explained by insufficient interfacial bonding between the NBR surface and the applied fluoroelastomer layer, likely due to the inherently low adhesion of the fluoroelastomer to the rubber substrate.

In contrast, the sample modified via the M3 method demonstrated a significant (nearly two orders of decimal

Table 7. Friction coefficient and abrasion of as-received and modified rubbers

Grinding metal	Rubber	Abrasion, m^3/TJ		Friction coefficient	
		Abrasion cycles			
		200	3000	200	3000
SS*	as-received NBR	0.046	0.043	0.92	0.90
CrNi**	as-received NBR	0.032	0.027	0.93	0.89
SS	NBR-M1	0.048	–	0.95	–
CrNi	NBR-M1	0.027	–	1.55	–
SS	NBR-M2	0.045	–	0.80	–
CrNi	NBR-M2	0.028	–	1.41	–
SS	NBR-M3	0.0005	0.0004	0.50	0.49
CrNi	NBR-M3	0.0004	0.0003	0.47	0.45

* SS is stainless steel grade 25;

** CrNi is chromium-nickel steel.

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[3] ISO 37:2024. Rubber, vulcanized or thermoplastic—Determination of tensile stress-strain properties.

[4] ASTM D2240-2015 (R 2021). Standard test method for rubber property. Durometer hardness.

magnitude) improvement in abrasion resistance, decreasing from 0.046 m^3/TJ for the as-received NBR to just 0.005 m^3/TJ. This enhancement is attributed to the formation of a uniform fluoropolymer-based surface coating as a result of immersion in a fluoroplast F32L solution.

The application of the fluoropolymer coating also led to a marked reduction in the initial friction coefficient against metal substrates. This effect is primarily associated with a decrease in adhesive interaction at the sliding interface, which is a well-known characteristic of perfluorinated polymer surfaces. The deposited surface layer exhibits properties similar to those of highly fluorinated polymers, which are distinguished by their extremely low surface energy and exceptional anti-adhesive performance. Fluoropolymers, including the one used in this study, typically demonstrate ultra-low friction coefficients (as low as 0.05 against steel).

The influence of each surface treatment method on the mechanical properties of NBR according to collected and analyzed mechanical test data is summarized in Table 8.

Table 8. Mechanical properties of the initial and modified rubbers

Properties	As-received NBR	NBR-M1	NBR-M2	NBR-M3
Tensile modulus at 100%, MPa	2.05	2.68	3.03	3.82
Tensile modulus at 300%, MPa	6.83	8.29	8.50	9.87
Tensile strength, MPa	10.17	10.81	10.61	12.29
Elongation at break, %	580	530	490	490
Relative residual elongation, %	9	12	9	6
Hardness (Shore A), a.u.	57	61	63	68

As shown in Table 8, the mechanical properties of surface-treated NBR—including tensile modulus at 100% and 300% strain, as well as tensile strength and hardness—show improvements compared to the as-received NBR. For samples modified using methods M1 and M2, the tensile strength remains comparable to that of the unmodified rubber, indicating that the bulk integrity of the elastomeric matrix is preserved. Notably, the hardness of NBR-M1 and NBR-M2 samples increased by 4 and 6 Shore A units, respectively. This change can be attributed to the formation of a stiffer surface layer due to the application of the fluoroelastomer-based composition. However, this increase in hardness is superficial in nature and not associated with a measurable increase in cross-link density: no experimental data (e.g., swelling tests or NMR-based analysis) confirm changes in the network structure of the vulcanizate. For the M3-treated rubber samples, which were immersed in a fluoroplast solution, the modulus at 100% and 300% strain increased by 86% and 44%, respectively; the tensile strength improved by 20%; and the hardness rose by 9 Shore A units compared to the as-received NBR. These findings are in line with previous studies suggesting that increases in hardness correlate with higher values of elastic modulus.

The observed hardness enhancement—particularly in the NBR-M3 sample—is due to the presence of a rigid fluoroplastic surface coating, which reduces the indentation depth during Shore A hardness measurements. This effect, which is mechanical rather than chemical, does not reflect an actual increase in cross-link density within the rubber bulk. Accordingly, the abrasion disc penetrates less deeply into the harder surface layer, which contributes to improved wear resistance. Moreover, it is well known that the friction coefficient of harder rubber is generally lower than that of softer rubber when sliding against rough surfaces [28]. Therefore, the observed decrease in friction for M3-modified samples is consistent with the formation of a rigid, low-energy fluoropolymer surface layer.

The depth and uniformity of the applied surface coating in the M3-modified NBR were evaluated using Scanning Electron Microscopy combined with Energy Dispersive X-ray Spectroscopy (SEM-EDX), as shown in Figs. 1 and 2.

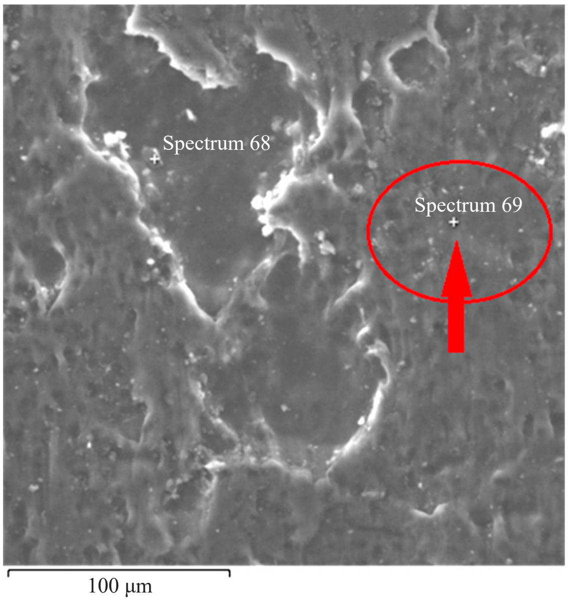
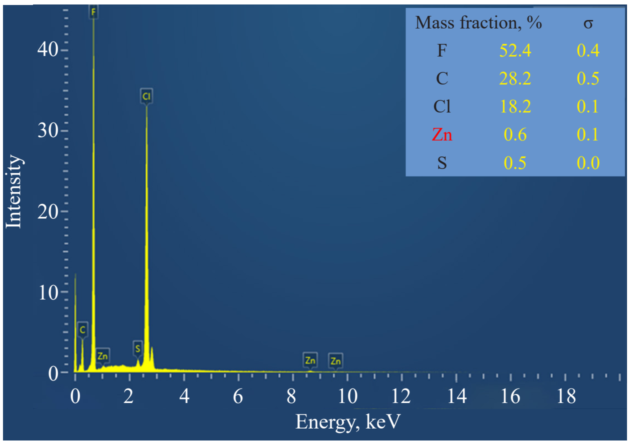


Fig. 1. SEM micrographs of NBR rubber after M3 modification (NBR-M3)



Mass fraction, %		σ
F	52.4	0.4
C	28.2	0.5
Cl	18.2	0.1
Zn	0.6	0.1
S	0.5	0.0

Fig. 2. Energy dispersive X-ray analysis (EDX) spectrum of NBR-M3

The EDX spectrum of the NBR rubber surface after immersion in 1,1,2-trifluoro-1,2,2-trichlorethane was used for quantitative elemental analysis (Figs. 1 and 2). The analysis confirmed the presence of fluorine (52.4 ± 0.4 at. %) and chlorine (18.2 ± 0.1 at. %) in the surface layer of the polymer. Moreover, pointwise EDX measurements indicated a uniform distribution of these halogen elements across the surface, suggesting that the applied fluoropolymer coating is continuous and well-adhered (Fig. 2).

CONCLUSIONS

In this work, new methods of enhancing the surface properties of NBR rubber through fluoropolymer-based coatings are proposed and evaluated. The study considered three surface treatment approaches. Methods M1 and M2 involved applying an elastomeric composition based on FKM-32 and a vulcanizing agent to the rubber surface, with method M2 additionally including a pre-swelling step in MEK for 10 min to facilitate deeper penetration of the composition into the rubber matrix. Method M3 consisted of immersing the rubber samples in a 10% solution of fluoroplast F32L in 1,1,2-trifluoro-1,2,2-trichloroethane for 6 h, resulting in the formation of a rigid surface layer.

Experimental results showed that, regardless of the use of pre-swelling in solvent, methods M1 and M2 had limited influence on improving wear resistance or reducing friction. This limited performance is likely related to insufficient adhesion of the applied elastomeric layer to the NBR substrate. In contrast, surface treatment via method M3 led to a substantial enhancement in both tribological and mechanical properties, including a significant reduction in the friction coefficient and wear rate, as well as increases in modulus and hardness. The improved performance of M3-treated samples is attributed to the presence of a continuous fluoropolymer coating, which modifies the surface characteristics without affecting the bulk rubber structure.

As confirmed by SEM-EDX analysis after drying and washing, the presence of fluorine and chlorine atoms in the surface layer indicates that the applied coating remains intact and is responsible for the observed improvements in performance.

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Authors' contributions

K.V. Sukhareva—research concept, experimental work, processing experimental data, writing original draft.

I.A. Mikhailov—research concept, writing original draft, processing experimental data.

B.B. Khaidarov—correction of the research concept, processing experimental data.

A.D. Buluchevskaya—experimental work and editing.

I.N. Burmistrov—correction of the research concept.

The authors declare no competing interests.

REFERENCES

1. Ning K., Lu J., Xie P., Hu J., Huang J., Sheng K. Study on Surface Modification of Silicone Rubber for Composite Insulator by Electron Beam Irradiation. *Nucl Instrum Methods Phys Res B*. 2021;499:7–16. https://doi.org/10.1016/j.nimb.2021.04.019
2. Song J., Vancso G.J. Effects of Flame Treatment on the Interfacial Energy of Polyethylene Assessed by Contact Mechanics. *Langmuir*. 2008;24:4845–4852. https://doi.org/10.1021/la7035532
3. Romero-Sánchez M.D., Pastor-Blas M.M., Martín-Martínez J.M., Zhdan P.A. Watts J.F. Surface Modifications of a Vulcanized Rubber Using Corona Discharge and Ultraviolet Radiation Treatments. *J Mater Sci*. 2001;36:5789–5799. https://doi.org/10.1023/A:1012999820592
4. Martínez L., Álvarez L., Huttel Y., Méndez J., Román E., Vanhulsel A., Verheyde B., Jacobs R. Surface Analysis of NBR and HNBR Elastomers Modified with Different Plasma Treatments. *Vacuum*. 2007;81:1489–1492. https://doi.org/10.1016/j.vacuum.2007.04.025

5. Kavc T., Kern W., Ebel M.F., Svagera R., Pölt P. Surface Modification of Polyethylene by Photochemical Introduction of Sulfonic Acid Groups. *Chemistry of Materials*. 2000;12:1053–1059. https://doi.org/10.1021/cm991158p
6. Nuzaimah M., Sapuan S.M., Nadlene R., Jawaid M. Effect of Surface Treatment on the Performance of Polyester Composite Filled with Waste Glove Rubber Crumbs. *Waste and Biomass Valorization*. 2020;12(2). https://doi.org/10.1007/s12649-020-01008-2
7. Lu X., Wang J., Cai S., Niu B., He Q., He X. Improving Thermo-oxidative Stability and Mediums Resistance of Nitrile Rubber via Surface Superhydrophobic Modification. *J. Appl. Polym. Sci*. 2022;139(17). https://doi.org/10.1002/app.52016
8. Yang Q., Chen S., Gao S., Wan S., He X. Improving Thermal-oxidative Stability of Nitrile Butadiene Rubber Composites by Surface Modification of Zirconium Phosphate. *Polym. Compos*. 2023;44:505–514. https://doi.org/10.1002/pc.27113
9. Wu Y.M., Liu J.Q., Cao H.T., Wu Z.Y., Wang Q., Ma Y.P., Jiang H., Wen F., Pei Y.T. On the Adhesion and Wear Resistance of DLC Films Deposited on Nitrile Butadiene Rubber: A Ti-C Interlayer. *Diam Relat Mater*. 2020;101. https://doi.org/10.1016/j.diamond.2019.107563
10. Zhou Z., Han Y., Qian J. Improving Mechanical and Tribological Behaviors of GLC Films on NBR under Water Lubrication by Doping Ti and N. *Coatings*. 2022;12. https://doi.org/10.3390/coatings12070937
11. Nudelman Z.N., Dontsov A.A., Novitskaya S.P. *Ftorelastomery* (*Fluoroelastomers*). Moscow: Khimiya; 1988. 240 p. (In Russ.).
12. Dontsov A.A., Lozovik G.Ya., Novitskaya S.P. *Khlorirovannye polimery* (*Chlorinated Polymers*). Moscow: Khimiya; 1979. 232 p. (In Russ.).
13. Tutorsky I.A., Potapov E.E., Shvarts A.G. *Khimicheskaya modifikatsiya elastomerov* (*Chemical Modification of Elastomers*). Moscow: Khimiya; 1993. 304 p. (In Russ.).
14. Nudelman Z.N. *Ftorkauchuki: osnovy, pererabotka, primenenie* (*Fluororubbers: Fundamentals, Processing, Application*). Moscow: PIF RIAS; 2007. 383 p. (In Russ.).
15. Nudelman Z.N., Galil-ogly F.A., Novikov A.S. *Ftorkauchuki i reziny na ikh osnove* (*Fluororubbers and Rubbers Based on Them*). Moscow: Khimiya; 1966. 234 p. (In Russ.).
16. Adov M.V., Zuev A.V., Pichkhidze S.Ya., Yurovsky V.S. Application of Fine Rubber Powder Based on Chloroprene Rubber in the Formulation of Rubber Compounds Based on This Rubber. *Kauchuk i rezina*. 2010;4:25–27 (in Russ.).
17. Pastor-Blas M.M., Martín-Martínez J.M. Different Surface Modifications Produced by Oxygen Plasma and Halogenation Treatments on a Vulcanized Rubber. *J. Adhes. Sci. Technol.* 2002;16:409–428. https://doi.org/10.1163/156856102760067190
18. Abbott S.G., Brewis D.M., Manley N.E., Mathieson I., Oliver N.E. Solvent-Free Bonding of Shoe-Soling Materials. *Int. J. Adhes.* 2003;23:225–230. https://doi.org/10.1016/S0143-7496(03)00025-3
19. Daniel P., Thian H.Ng., Heam K.T., Roger L., Matt J.C. The effects of chlorination, thickness, and moisture on glove donning efficiency. *Ergonomics*. 2021;64(3). https://doi.org/10.1080/00140139.2021.1907452
20. Khan M.S., Heinrich G. PTFE-Based Rubber Composites for Tribological Applications. *Advanced Rubber Composites*. 2010:249–310. https://doi.org/10.1007/12_2010_98
21. Belov N.A., Alentiev A.Y., Bogdanova Y.G., Vdovichenko A.Y., Pashkevich D.S. Direct Fluorination as Method of Improvement of Operational Properties of Polymeric Materials. *Polymers* (*Basel*). 2020;12. https://doi.org/10.3390/polym12122836
22. Qiang G., Changou P., Pengwei X., Mingliang P., Peng L. Fluorination of nitrile-butadiene rubber without gelation via radical graft polymerization in presence of chain transfer agent. *European Polymer Journal*. 2021;151. https://doi.org/10.1016/j.eurpolymj.2021.110442
23. Gao J., Dai Y., Wang X., Huang J., Yao J., Yang J., Liu X. Effects of Different Fluorination Routes on Aramid Fiber Surface Structures and Interlaminar Shear Strength of Its Composites. *Appl Surf Sci.* 2013;270:627–633. https://doi.org/10.1016/j.apsusc.2013.01.099
24. Qiang G., Changou P., Siwei Sh., Pengwei X., Mingliang P., Peng L. Facile fluorination of nitrile-butadiene rubber via olefin cross metathesis. *Polymer*. 2021;217. https://doi.org/10.1016/j.polymer.2021.123455
25. Yang X., Yang C., Nie M. Industrial Preparation of Self-Lubricating Polyurethane via Direct Fluorination with Gaseous Fluorine. *ACS Omega*. 2022;7:28388–28395. https://doi.org/10.1021/acsomega.2c03019
26. Belov N.A., Pashkevich D.S., Alentiev A.Y., Tressaud A. Effect of Direct Fluorination on the Transport Properties and Swelling of Polymeric Materials: A Review. *Membranes*. 2021;11(9). https://doi.org/10.3390/membranes11090713
27. Kharitonov A.P. Direct Fluorination of Polymers – From Fundamental Research to Industrial Applications. *Prog Org Coat.* 2008;61:192–204. https://doi.org/10.1016/j.porgcoat.2007.09.027
28. Mostafa A., Abouel-Kasem A., Bayoumi M.R., El-Sebaie M.G. Insight into the Effect of CB Loading on Tension, Compression, Hardness and Abrasion Properties of SBR and NBR Filled Compounds. *Mater Des.* 2009;30:1785–1791. https://doi.org/10.1016/j.matdes.2008.07.037

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