ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 3, pp. 565–577. © Pleiades Publishing, Ltd., 2009.
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Fluorinated Rubber with Improved Tribotechnical Properties

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Received February 1, 2008

Abstract—The systemized experimental results of volume and surface modification of industrial rubbers of different purpose with the fluorine-containing compounds is described in the survey. The elastomer surface modification with fluorine mixed with inert gases and by combined techniques using the “surface-prescription” approaches is the most interesting. The significant improvement of tribotechnical rubber characteristics was found as a result of chemical structure of the surface layer transformation and also by its morphology changing.

DOI: 10.1134/S1070363209030384

INTRODUCTION

The tendencies of developing fundamental works and technologies of obtaining new elastomer materials with a complex of positive physical and chemical properties show, that traditional methods of synthesis have exhausted themselves in many respects and the probability of appearance of elastomers with characteristics, which substantially exceed the known level, decreased considerably. Nowadays another direction of obtaining elastomers is intensively developing: the modification of available caoutchoucs and rubbers [1–11]. Such an approach allows qualitatively new materials to be obtained on the basis of known elastomers with improved physical, chemical and operational properties.

Rigorous conditions of exploitation of general mechanic rubber products, including in friction units (high velocities, high temperatures, chemically aggressive and abrasive active media, tensely deformed state), put forward increased requirements of wearing capacity of rubbers, rubbers on the basis of fluoroelastomer fitting this demand to a greater extent. Their distinctive features, due to specific chemical structure, are a high heat resistance and chemical stability, good physical and mechanic properties [12, 13]. At the same time, complicated technologies of obtaining, a low frost resistance and a considerable cost in comparison with other elastomers make the problem of obtaining fluorine-containing elastomers by other methods actual. Among them the modification of elastomer surface by fluorinating and blending reagents, and also combined methods of modification with the use of “prescribed” approaches, are of special interest [14, 15].

Volumetric and Surface Fluorination of Elastomers

In the early experiments on fluorination, performed with caoutchoucs [16], the samples were directly treated with molecular fluorine. Under these conditions the reactions occur vigorously and often with inflammation, that is why the fluorinating agent was diluted with an inert gas in order to soften the conditions. In all cases fluorine was found to add by the double bond and also to replace hydrogen atoms. However, the obtaining of great extent of fluorination failed and a considerable destruction of polymers was noted.

In [18] a technological procedure of elastomer fluorination with antimony pentafluoride is recommended, which is essentially less active than fluoride. The electron-microscopic study of the rubber surface showed that on fluorinating in a gas phase using SbF_5 the rubber surface is not destroyed, but microscopic mounds, which are located uniformly and closely, appear on it. The expense of SbF_5 in the gas-phase procedure is small (100–140 g m^{-2}), the manufacture of fluorinated product is not accompanied by liquid and gaseous blowouts. A dry mixture of sodium salt of antimonous acid and of calcium fluoride is the waste product of the manufacture. As a result of such treatment the friction coefficient decreases by a factor of 3 on the average, the temperature in the friction zone decreases by factors of 2–3, and the shearing force decreases by factors of 5–10 in comparison with rubber with nonfluorinated surface.

Antimony pentafluoride was also used in [23, 24]. Moreover, the treatment by sulfur tetra fluoride [22], fluoric nitrogen compounds [8], and halogen fluorides [25] was applied in order to improve the elastomers characteristics. The use of chlorine, bromine, and iodine with this aim was less effective [19–21].

In [17] the rubber fluorination on the basis of butadienenitrile caoutchouc was carried out with the use of xenon difluoride. The modification resulted in the increase of oil resistance and a decrease of rubber friction coefficient. The study of the surface structure of fluorinated rubbers (the X-ray structure analysis) showed the presence of $–CH_2–CHF–CH_2–$, $–CHF–CH_2–CHF–$, and –CHF–CHF–CHF– fragments on the rubber surface; the depth of fluorination was 8–9 μm.

On the basis of the discovered effect of anomalous low friction [26, 27] the plasma chemical method of modification of elastomer surface was developed. The main point of the method consists in the formation of thin antiadhesion layers on the rubber surface by the inoculation in the glow discharge plasma of fluorine-containing monomers with a low surface energy and low adhesive activity [28, 29].

In another procedure [30] before vulcanization the rubber mixture is moistened with organofluoric compounds (e.g. “fluorine kerosene”), dried, vulcanized, and treated in the glow discharge. Then the product is moistened with an emulsion of organofluoric compound, dried, and treated in the glow discharge again.

In [31] plasmochemical modification was carried out using tetrafluoroethylene, carbon tetra fluoride, and argon as plasma forming gases in order to improve antifriction properties of rubbers and also their chemical stability. The treatment by plasma in the tetrafluoroethylene medium allows the chemical stability of rubbers based on ethylene-propylene caoutchouc (SKEPT) to be slightly increased. Chemical structure of tetrafluorethylene polymerized on the rubber surface was found by the methods of electron and IR spectroscopy to have differences from the structure of tetrafluoroethylene, which is polymerized on another support. A greater increase in the chemical stability was achieved by the treatment of SKEPT rubber in argon plasma. The main result of these three types of plasma treatments was the decrease in the friction coefficient of rubbers, based on both ethylene-propylene caoutchouc and butadiene-nitrile caoutchouc (SKN). Except for SKN treated with plasma in CF_4 medium, this decrease appeared to be reversible: the starting friction coefficient recovered after 500–1000 product rotation cycles, evidently because of the deformation and destruction of the modified layer (Fig. 1a).

The method of metallization of rubber surface with aluminum with its previous modification in a glow discharge was advanced [32]. Spraying aluminum on the modified rubber surface is carried out at the residual pressure 10^{-5} mm Hg. The thickness of thus obtained aluminum film on the rubber surface is 0.3 μm. Metallization of rubber surface substantially decreases the friction force (by factors of 2–5) and the temperature in the contact zone (by 100°C), however, the problem of maintaining the integrity of the metal surface layer upon the deformations is still actual.

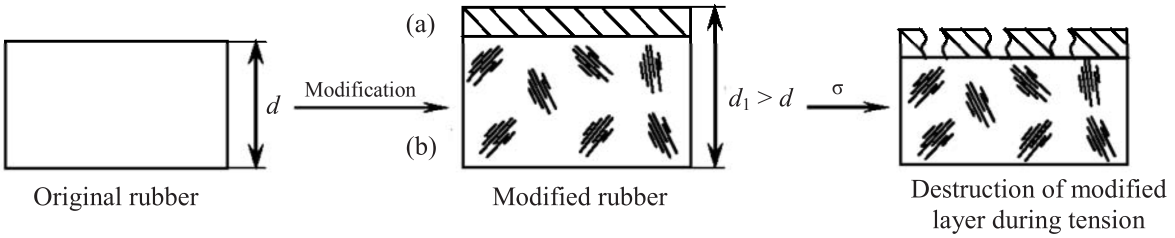

Fig. 1. Scheme of elastomer modification by (a) depositing a surface fluorinated layer and (b) introducing ingredients into the rubber mixture; (σ) is the tensile force.

In order to decrease the kinematic friction coefficient and the wear intensity, antifriction polymer coatings are deposited on the rubber compressing elements. Fluorolon and polyamide–imide varnishes, which possess good antifriction and mechanic characteristics, are used as a coating. The coating is hardened at the temperature 145°C with regard to the highest possible heat-resistance of rubbers of the nitrile caoutchoucs. The use of coatings of polyamide-imide varnishes of optimized composition allows an essential improvement of tribological characteristics of mobile compressing elements [33].

In order to increase the resistance to wear of the fluoroelastomer products, the elastomer is suggested to be treated with γ-aminopropyltriethoxysilane (the expense 0.005–0.006 ml cm^{-2}) with the following thermostating at 200–250°C during 24 h [34].

The compositions containing 30–210 mass parts of graphite per 100 mass parts of caoutchouc, a vulcanizing agent, and a solvent are recommended to be used as antifriction coatings. The composition is deposited on the vulcanizate and then is vulcanized repeatedly with the inoculation to its surface. The thickness of the obtained coating is ~110 μm. Such a treatment favors not only a decrease in the rubber friction coefficient, but also an increase in its oil resistance and resistance to organic solvents [35].

Antifriction elastomer compositions, containing 11–37% of finely dispersed polytetrafluoroethylene were advanced [36]. The coating is deposited on the rubber surface, and then it is thermostated at 150°C for 10 min. The thickness of the coating is 0.05–0.1 mm. In order to increase the antifriction characteristics, fluorine containing polymer is used as a polymer binder and after thermostating an extra treatment is carried out (thermic stroke at 380–450°C during 1–6 s) [37]. The presence of a transition zone was discovered by electron microscopy method on the interface between the coating and the elastomer base and also an increased quantity of fluoroplastic on the rubber surface with coating, which defines the improvement of antifriction characteristics of such systems.

Therefore nowadays there are various approaches to the surface and volumetric (Fig. 1b) modification of products of elastomers by fluorine containing compounds. However, many of the listed methods are notable for an increased labouriousness, the elimination of toxic products during elastomer modification, a complex technical equipment of the method. Moreover, a sufficiently high level of antifriction characteristics and other properties is not always achieved.

On the basis of systematic researches, which were carried out jointly with our partners (OAO “NIIEMI,” OAO “Balakovoresinotehnika,” REAM, GNC “Prikladnaya Khimiya,” Ural Factory RTI and others), the possibility of creating a sufficiently efficient technology of treatment of rubber surfaces with fluorine in the mixture with an inert gas was substantiated [38]. Previously [14–17, 39] the efficiency was shown of using elemental fluorine for the modification of polymer material surface, elastomers among them [40, 41]. The process of treatment consists in the following. The product is kept in a gaseous reagent in a sealed reactor of stainless steel. Then the evacuation is carried out in order to remove the products of the reaction and unreacted fluorine and the pressure is brought to the atmospheric pressure. Gaseous products of the reaction and ureacted fluorine are neutralized as they leave the reactor in the column with a chemical absorbent; liquid wastes are absent. So the ecologically and technically safe technology is attained [42].

In the advanced method the fluorine containing layer results from the reactions occurring directly in the surface layer of the elastomer, which removes the problem of providing the adhesion. As the result of such a treatment the product obtains a set of positive characteristics such as ozono-, bio- and chemical resistance to oxidants and aggressive liquids, a low friction coefficient, a low rate of ingredient migration, the stability to tension without the loss of continuity of fluorinated layer and a number of other characteristics (Fig. 2).

Moreover, the developed method of surface modification is compatible with methods of prescribed modification, the use of effective fluorine containing ingredients among them advanced by us together with GNC “Prikladnaya Khimiya” and REAM firm.

The special feature of rubber fluorination is a high rate of the reactions, defined by an essential quantity of unsaturated bonds in a macromolecular chain, along which atoms of fluorine add easily, and a rather high diffusion rate of the reagent in rubber. By means of reagent diffusion, which can be in the form of molecular F_2 as well as in the form of $F^{\cdot}$. radical, the reaction of fluorination is spread into the volume of rubber mixture [16]. As the result of chemical modification of vulcanized rubber surface by gaseous

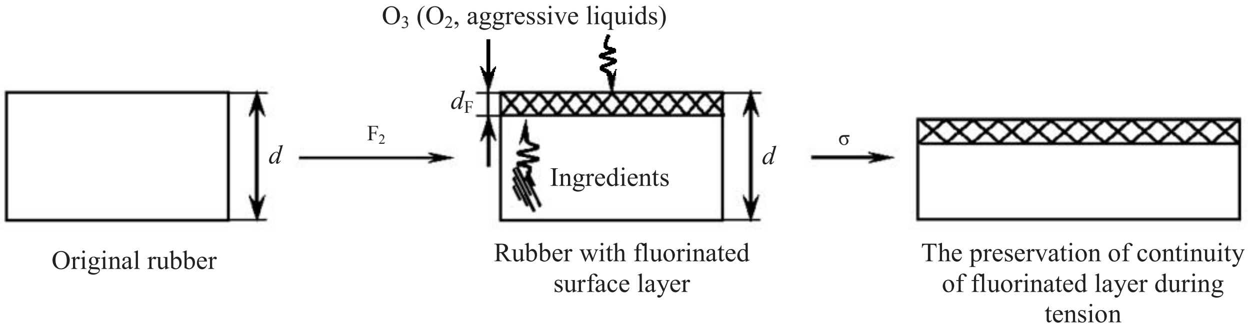

Fig. 2. Scheme of rubber surface modification by heterogeneous fluorination method.

fluorine the obtained fluorinated layer differs from the original rubber in its chemical structure and composition.

Upon surface modification with gaseous fluorine the thickness of rubber sample does not change (Fig. 2), and the modified surface layer and volumetric phase of rubber represent the intrinsic whole unlike the modification by surface layer deposition (Fig. 1).

The thickness of fluorinated layer d_F (the shaded area in Fig. 2) in the case of surface modification of rubber by gaseous fluorine is a rather conventional concept because of the absence of distinct interface between this layer and volumetric phase of rubber. In the surface layer of modified rubber the concentration of "linked" fluorine is maximal at the surface and decreases smoothly when moving down into the material. Nevertheless, an evaluative calculation of d_F is possible depending on the degree and duration of fluorination [39].

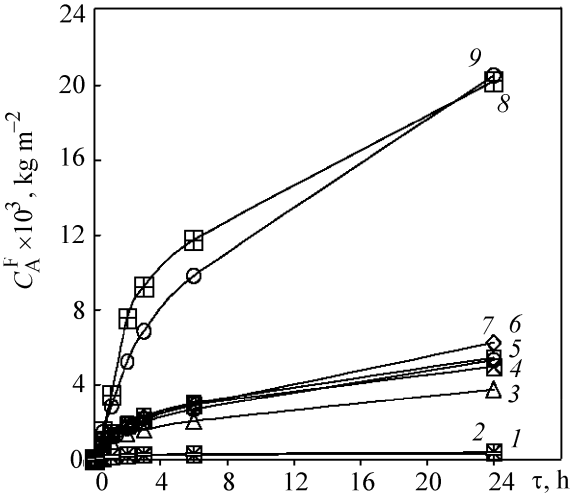

Fig. 3. Kinetic dependencies of caoutchouc fluorination degree: (*1*) SKF-26, (*2*) SKF-32, (*3*) BK, (*4*) SKD, (*5*) SKI-3, (*6*) SKEPT-60, (*7*) SKN-18+PHP, (*8*) BNKS-18A, and (*9*) SKN-26.

The obtained values of d_F for rubber based on butadienenitrile SKN-26 caoutchouc (8, 13, and 18 μm upon fluorinating for 3, 6, and 24 h respectively) are by an order of magnitude higher than the size of fluorinated layers, calculated for polyethylene of low density in operation [43]. This is defined by a substantial number of unsaturated bonds, of other reactive centers, and by greater fluorine diffusion coefficient in rubbers.

In order to estimate the contribution of individual ingredients of rubber mixture to the total rate and degree of rubber fluorination (the ratio of fluorine mass, reacted with the sample, to the area of its surface) the dependencies of fluorination degree on the duration of its treatment at a constant temperature (20°C) and fluorine concentration in fluorinating mixture (15 vol %) were studied. In this case the technological operations, that allow minimizing the destruction reactions, were varied.

Kinetic dependencies of the degree of fluorination of original uncured caoutchoucs on the duration of fluorination are given in Fig. 3; they are described by increasing curves with saturation.

The contents of fluorine in elastomers and ingredients were determined by the elemental analysis and gravimetric method. The lowest degrees of fluorination for the same time of modification are attained for the types CKF-32 and CKF-26 caoutchoucs (the most resistant to fluorine action). Average degrees of fluorination are typical for butyl rubber (BK), butadiene (SKD), isoprene (SKI-3), ethylene-propylene (SKEPT), neopren (PHP) caoutchoucs. The highest degree of fluorination is attained for butadiene-

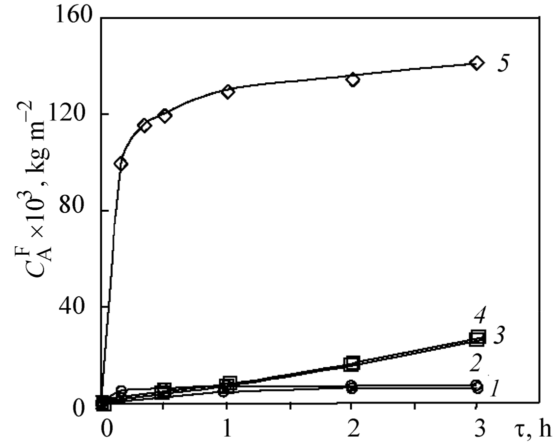

Fig. 4. Kinetic dependencies of fluorination of rubber mixture ingredients: (*1*) caoutchouc SKN-26 (for comparison sake), (*2*) technical carbon, (*3*) stearic acid, (*4*) dibutyl sebacate, and (*5*) MgO.

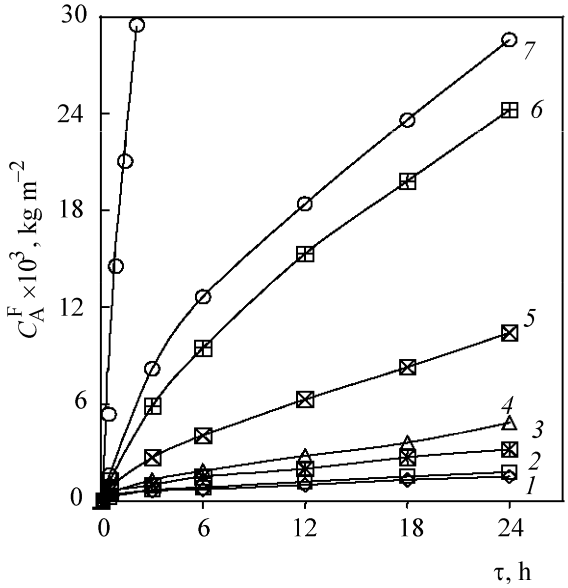

Fig. 5. Kinetic dependencies of rubber fluorination degree: (*1*) SKF-26, (*2*) SKF-32, (*3*) BK, (*4*) SKEPT, (*5*) SKI-3 + SKD + SKMS-30 (modified silicon caoutchouc), (*6*) PHP + SKN-18, (*7*) SKN-26, and (*8*) NC (natural caoutchouc).

nitrile caoutchoucs SKN-18 and SKN-26. The differences in the rate and fluorination degree of the samples are defined by the chemical structure of caoutchoucs. As macromolecules of caoutchouc surface layer become saturated with fluorine the stability of elastomer to fluorine increases and further fluorination of caoutchouc is determined by fluorine diffusion into the volumetric phase of caoutchouc. Thus, not only the presence of double bonds and mobile hydrogen atoms in a macromolecule influences the degree of fluorination, but also the rate of fluorine diffusion in the volume of caoutchouc, which is determined by its structure, in particular, by the degree of crystallinity.

The kinetic dependencies of fluorination of other ingredients of rubber mixture are given in Fig. 4.

The degree of fluorination of such ingredients as carbon, MgO, stearic acid, dibutyl sebacate for the same duration of fluorination is seen to be higher than for caoutchoucs, into which they are added.

Under similar conditions kinetic dependencies of the degree of fluorination of vulcanized rubbers on the duration of fluorination were obtained (Fig. 5).

By their degree of fluorination obtained at the same time of modification the rubbers fall in the same sequence as corresponding caoutchoucs: rubbers on the basis of SKF-26 ≈ SKF-32 < BK < SKEPT < SKI-3 + SKD + SKMS-30 < PHP + SKN-18 < SKN-26 < NC (natural caoutchouc).

The degree of fluorination of caoutchoucs and rubbers at the same and optimal duration of fluorination (1–3 h) for the majority of practical cases is lower than the degree of fluorination of other ingredients of rubber mixture (MgO, technical carbon, dibutyl sebacate, stearic acid). At the same time, these components influence the obtained degree of rubber fluorination to a very small extent because the fluorination of these ingredients is realized mainly at the expense of diffusion of fluoridizer through the rubber surface layer. Consequently, when the rubber surface is fluorinated as a multicomponent system, the main ingredient, which undergoes the action of fluorine, is caoutchouc, and its chemical nature is the first to define the degree of rubber fluorination.

Concerning volumetric modification, which consists in introducing antifriction fillers into the rubber composition [44], it is widely applied for improving the rubber wear resistance because of the simplicity of the method and its rather high efficiency. Molybdenum disulfide, graphite, silicon nitride, carbon fiber materials, polytetrafluoroethylene and others [45–48] are usually used as antifriction rubber modifiers, which allows a prolongation of the effect of friction coefficient decrease and of a shift effort on the product

Table 1. Some properties of fluorine containing modifiers

Modifier number	Modifier	Appearance	MM_{av}	Density, g cm^{-3}	Melting point, °C
1	Fluorinated polyether	Transparent viscous liquid	2200	1.72	from –35 to –45
2	Fluorinated alcohol telomere	White amorphous substance	800	1.79	from 105 to 110
3	Polytron (suspension of polytetrafluoroethylene micro particles)	Transparent yellowish suspension	–	1.02	from –49 to –53

operation. The introduction of low-molecular organofluorine compounds into the formulation of rubber mixtures is also efficient [49]. Even small quantities of fluorine organic compounds (1–3 mass parts per 100 mass parts of caoutchouc), acting as interstructure modifiers, are capable of improving substantially the characteristics of rubbers [48, 49]. Some characteristics of modifiers under study are shown in Table 1.

Morphology of the Surface Layer of Fluorinated Elastomers

When the surface of fluorinated elastomer composition was microscopically investigated (a Stereoscan-360 electron microscope of "Cambridge Instruments" firm and a "Polam P-312" polarization microscope), the sample surface was found to become more rough as the duration of fluorination increases. Such a change of surface layer morphology upon fluorination is conditioned by a partial destruction of elastomer and of some other ingredients (at different rates) with simultaneous adding fluorine to the double bonds, and this shows itself in the microphotographs as an increase in the quantity and relative part of structural micro heterogeneities.

The detailed study of morphological changes of rubber surface resulting from surface fluorination was carried out with the rubber samples based on caoutchoucs SKN-26, SKEPT and rubber-textile linen–tympan of Bottsher Top 4800 type with the use of an electron microscope. The photograph of reference and fluorinated for 3 hours rubber samples are given in Figs. 6, 7, and 8.

Essential morphological changes are observed in the photographs of all the fluorinated rubber surfaces. It is legitimated to suppose that they are caused by different rate and depth of fluorination in amorphous and crystal areas of elastomer and also by an increase in the mole volume of fluorinated surface layer, as it was in the case of fluorinating polyethylene [50]. At the same time the character and intensity of these changes seem to be defined by the nature of elastomer, the type and quantity of ingredients (first of all by fillers) of elastomer composition, and also by the method of vulcanization. So, the layered structures 2×3 μm in size, separated by hollows are observed in the surface layer of rubber on the basis of CKN-26 with white soot BS-50 and perlite fillers (Fig. 6). The

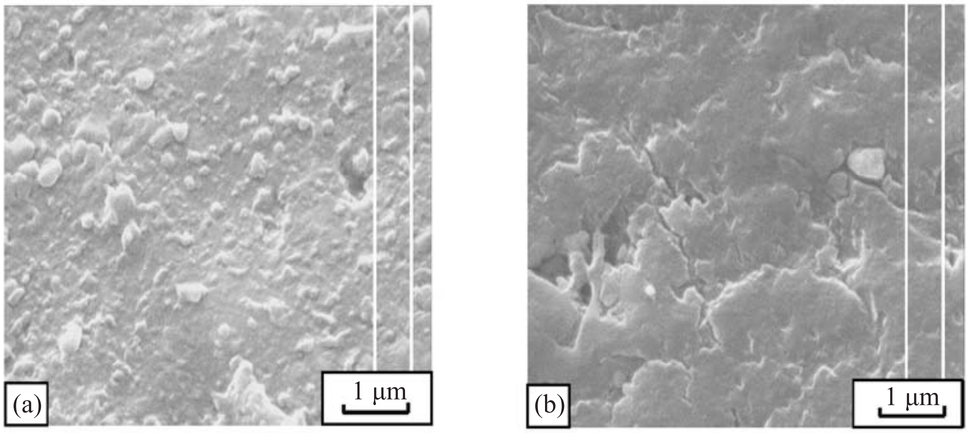

Fig. 6. The photographs of (a) reference and (b) fluorinated rubber samples of SKN-26. Magnification ×10000.

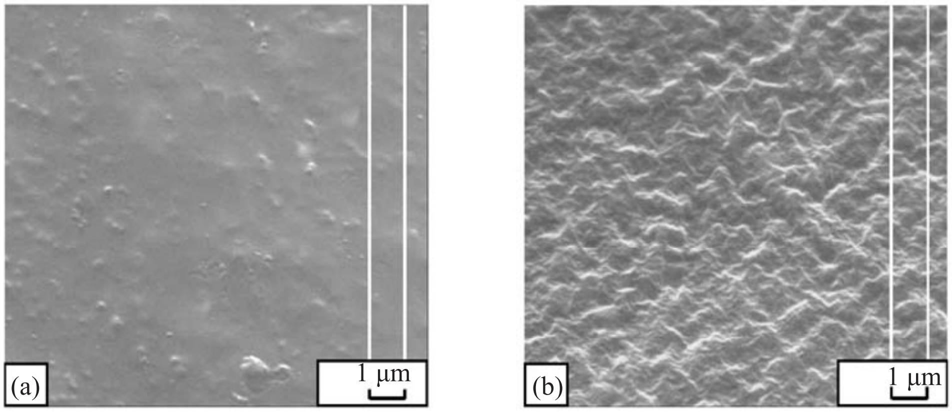

Fig. 7. The photographs of (a) reference and (b) fluorinated rubber samples of SKEPT. Magnification ×10000.

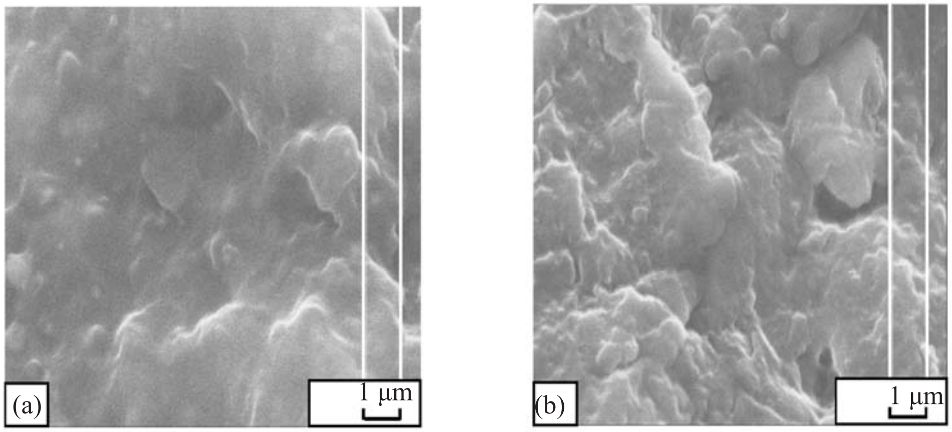

Fig. 8. The photographs of (a) reference and (b) fluorinated samples of rubber–fabric–tympan of Bottsher Top 4800 type. Magnification ×10000.

hollows are likely be associated with the layered nature of this type of rubber (this can be seen in the photograph of butt cut, Fig. 9) and with substantial destruction processes on fluorination in the regions between the layers.

When the rubber on the basis of SKEPT, which is close to polyethylene in its chemical nature, is fluorinated, its surface becomes wavy with waves 300–500 nm in size (Fig. 8) as can be seen from electron microscopic study. Such a character of morphological changes of the surface is caused by rubber flexibility, which makes possible the relaxation of tension in a fluorinated layer to a greater extent. The formation of wavy structures 200–300 nm in size is typical also in the case of fluorination of tympan rubber (Fig. 8), though the starting wave-like form of tympan rubber layer masks them to a certain extent.

Therefore, the surface fluorination of rubbers results in the transformation of not only chemical structure of the surface layer, but also of its morphology. And though the forming surface structures have nano- and micrometer dimensions, they should be taken into account when studying the friction mechanism in the “modified rubber–metal” couple.

Tribotechnical Characteristics of Fluorinated Elastomers

Mechanic rubber goods (collars, stuffing boxes and other sealing materials) operating in the kinetic friction regime along metallic surfaces must possess high wear resistance. One of the ways of decreasing the rubber wear and increasing their capacity for work is the decrease in the friction coefficient of general mechanic rubber goods.

The dependencies of friction coefficient K_{fr} on the test time for surface fluorinated and control samples are described by the falling down curves with saturation (Fig. 10) [40, 46].

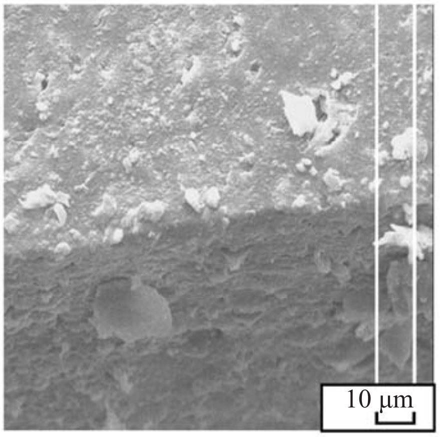

Fig. 9. The photograph of butt cut of SKN-26 rubber sample. Magnification ×10000.

The conditions of measurements: on an MTT-2 mechanism of front friction with metallic indentor (12 mm in diameter and 2 cm^2 in contact area), the force 4 kg given a rotation frequency of 120 rot/min without grease (dry friction). The relative error of measurements of K_{fr} is ±15%. K_{fr} is seen to decrease from originally high values of friction coefficient, which corresponds to the process of run-in of frictioning parts of rubbers and a counter body, and in about 15 minutes of experiment becomes constant in all cases.

In order to find out the influence of surface fluorination on the capacity for work resources of general mechanical rubber goods, the wear of fluorinated and control samples was evaluated in the conditions of prolonged tests (the wear was determined by the decrease in the sample mass for 3 h of test). The samples of rubbers under study based on SKN-26 and SKEPT were fluorinated for 3 h; the rubbers based on SKF-32 were fluorinated for 6 h. The results of the tests, given in Fig. 11, show a substantial increase in the rubber endurance: the wear of rubbers based on SKN-26 and SKEPT is decreased up to by a factor of 10, the wear of rubbers based on SKF-32 is decreased by a factor of 2.

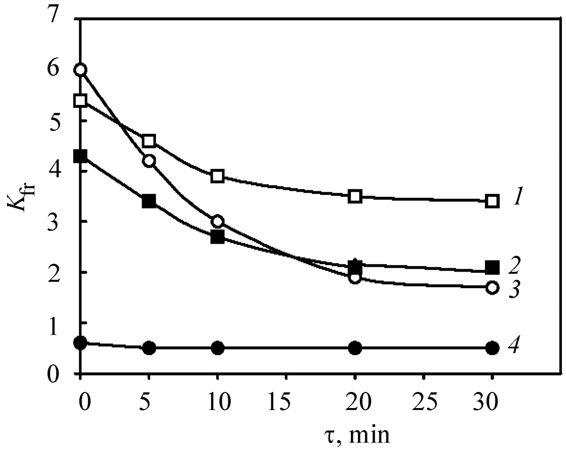

Fig. 10. Kinetic curves of the coefficient of friction of control and fluorinated rubber samples: (*1*) SKF-32, (*2*) SKF-32+F$_2$, (*3*) SKEPT, and (*4*) SKEPT+F$_2$.

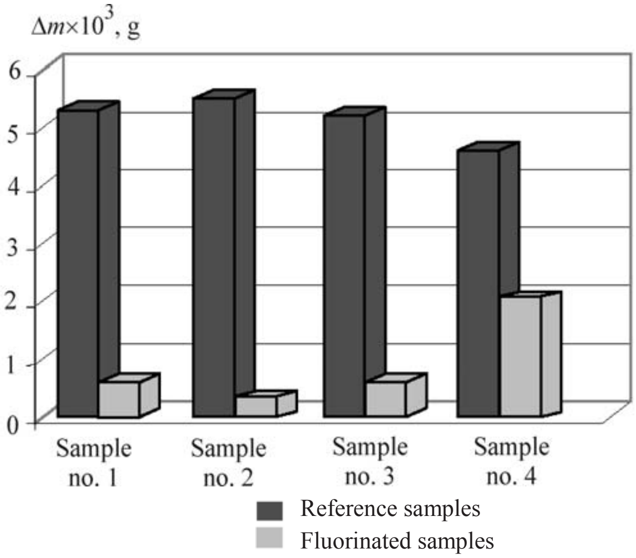

Fig. 11. The wear of control and fluorinated rubber samples during 3 h of their work. (Sample no. 1) SKN-26 (without plasticizer), (Sample no. 2) SKN-26 (10 mass p. of dibutyl sebacate), (Sample no. 3) SKEPT, and (Sample no. 4) SKF-32.

The positive effect of rubber treatment with fluorine is confirmed by the bench test statements of OAO ZIL and REAM firm and is protected by a patent [51].

The preparation of sample surface plays an important role in the achievement of maximum triboeffect of fluorination. The tests of rubber samles based on SKN-26 caoutchouc containing different quantities of dibutyl sebacate plasticizer and also of a control sample (without plasticizer) showed [52] that antifrictional properties of samples depend on the quantity of plasticizer, on the procedure and order of operations during rubber surface treatment. The introduction of 20% of plasticizer into the rubber mixture results in an essential decrease in K_{fr} (almost twice given $\tau = 0$ and more given $\tau = 30$ min) in comparison with the sample without plasticizer.

A comparison of the samples with various quantities of plasticizer showed, that the effect of surface fluorination depends on the surface pretreatment in many respects. Thus, if the sample containing 20 mass parts of dibutyl sebacate is fluorinated without surface pre-purifying with ethanol (without removing the migrated plasticizer from the sample surface), after fluorination the coefficient of friction and the rubber wear are almost the same for the nonfluorinated sample. It is believed that this is associated with a greater rate of fluorination of plasticizer, which is located on the surface, than of the plasticizer introduced into the rubber. This was confirmed by the experiments on separate fluorination of ingredients, which are the part of rubber based on SKN-26. The coefficient of friction of rubber samples, purified before the fluorination (the removal of excess of plasticizer migrated to the surface) decreases statically by factors of 2–3, and the sample wear decreases by factors of 3–4.

The introduction of volumetric fluorine containing modifiers slightly decreases the starting coefficient of friction (Table 2).

However, the rate of migration of modifiers from volumetric phase to the sample surface should be taken intoaccount. If the migration rate, which is determined by the diffusion coefficient, is small, in order to create a necessary concentration of modifier, reducing K_{fr}, on the sample suface more time is required, than in the case of greater migration rate. Volatility of modifier reflecting its capability of remaining on the product surface for a long time also is of a definite significance. The fluorination of the surface of all the samples (control and fluorine containing modifiers) in optimal conditions was found to allow a substantial decrease in K_{fr} (by factors of 2–6). This is defined by the nature of the sample surface layers resulting from fluorination, their chemical structure being close to that of fluoroelastomers. It is important that the fluorination effect is stable and is reproduced with a considerable number of samples of various rubber types.

A combined method of elastomer modification consisting in a joint use of volumetric modification

Table 2. Friction coefficient of friction of SKN-26 samples given various degree of fluorination

Modifier number (see Table 1)	The fluorination time, h	The fluorination degree, $C_A^F \times 10^3$, kg m^{-2}	Friction coefficient	
			without surface purification	after treatment with ethanol
Samples without modifier	0	0	1.2	1.4
	3	1.3	0.5	0.5
	6	2.5	0.4	0.6
	24	7.1	0.4	0.5
1	0	0	1.2	1.4
	3	1.4	0.5	0.6
	6	2.7	0.5	0.6
	24	7.5	0.3	0.6
2	0	0	1.1	1.0
	3	0.13	0.4	0.5
	6	0.29	0.4	0.6
	24	0.75	0.6	0.7
3	0	0	0.9	1.1
	3	0.13	0.2	0.4
	6	0.34	0.3	0.4
	24	0.71	0.3	0.5

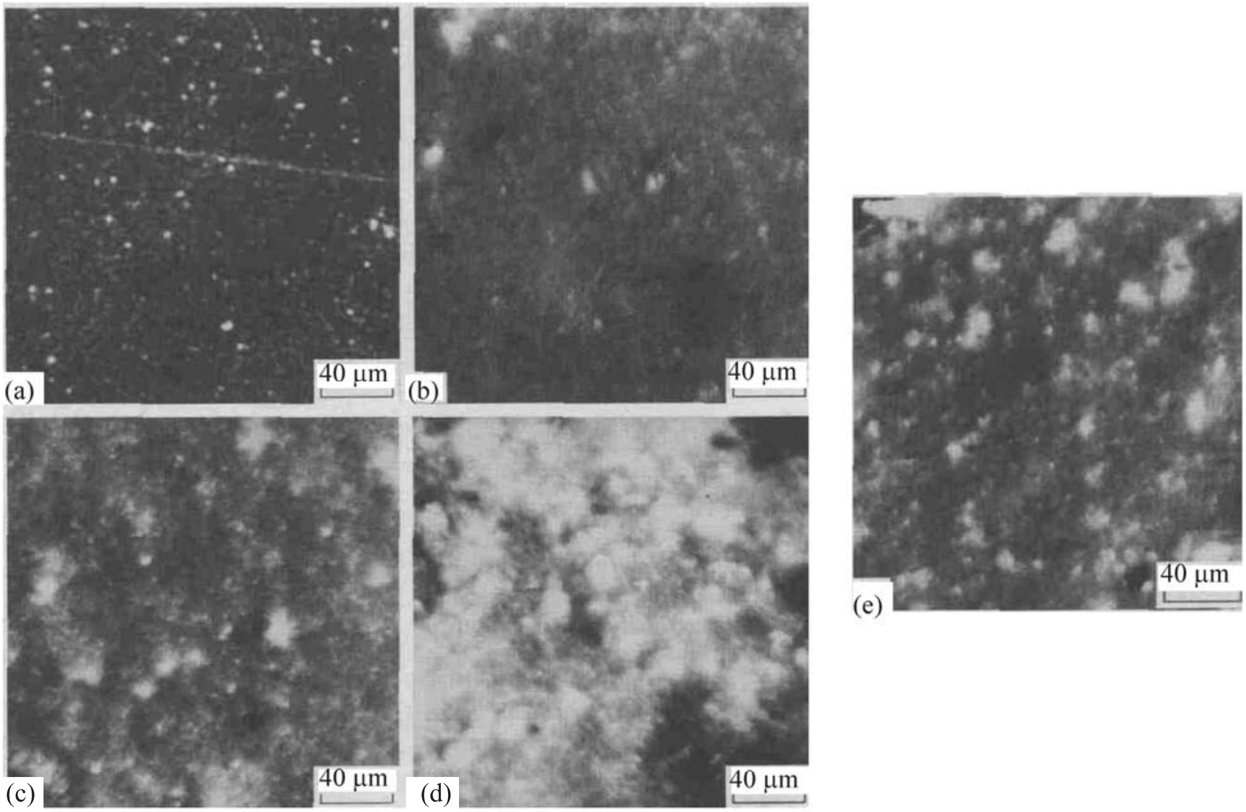

Fig. 12. The photos of surface of (a, d) control and (b, c, e) fluorinated rubber samples (a)–(c) before wear and (d, e) after wear

(introducing modifier into the rubber composition) and surface gase phase fluorination of elastomers provides a stable and substantial decrease in the coefficient of friction. The best results on decreasing the coefficient of friction were achieved for surface fluorinated elastomers containing micro dispersed polytetrafluoroethylene (8 mass parts), when the lowest value of K_{fr} is observed.

Fluorine containing modifiers possess a polyfunctional effect. The use of fluorine containing modifiers together with gas-phase fluorination allows not only the coefficient of friction and the wear to be decreased (up to three times in comparison with original samples), but also the durability and workability of mechanical rubber goods to be increased upon prolonged use [40, 49].

In order to reveal structural and morphological special features of fluorinated surface layers, the photomicrography was carried out by the method of phase contrast of starting and modified butadiene-nitrile caoutchouc SKN-26 samples before and after the tests on abrasion (Fig. 12).

The original sample is seen to have an essential damage of surface layers (the damaged areas have white colour and more "porous" structure in the photomicrography) whereas the surface layer of fluorinated sample is almost not abraded and damaged under the conditions of the experiment; this is defined by its increased microhardness and a decreased adhesive activity [41, 53].

The studies were carried out in order to determine the adhesive component of sliding friction in "rubber–metal" couple [54]. Adhesive contact force was characterized by the coefficient of sstarting friction (maximum value of the coefficient of friction in the first moment of movement), which was defined with the help of a scheme of the test for the shift by a tensile load with double-sided contact of metallic indenter with rubber samples overlapped [55]. Plates of 14 surface purity grade tool steel (plate of Iogansen), of 9 surface purity grade, and of the type D16 10 surface purity grade duralumin were used as identers.

The results of the tests are given in Fig. 13.

A substantial decrease in the coefficient of starting friction takes place for low degrees of rubber fluorination, corresponding to fluorination time of 5–10 min. Later, as fluorination goes on, the dependencies enter the stationary sites, i.e. the coefficient of starting friction almost ceases to depend on fluorination degree. Such a run of the curves seems to be accounted for by the fact that even in the starting period of fluorination a rather compact surface fluorinated layer is already formed on fluorine reacting with rubber macro molecules. Then, as fluorination process develops, its expansion into the depth of rubber takes place. For a substantial decrease in the adhesive "rubber–metal" interaction fluorination during 20–30 minutes is sufficient, as it is shown in Fig. 13. However, taking into account that the upper fluorinated layer can be abraded during exploitation [39], it is reasonable to carry out fluorination during 1–3 hours.

As a whole, a decrease in the coefficient of starting friction by factors of 3–6 is attained for all the indenters as the result of fluorination. To a greater extent it is observed for the plate of stainless steel with 14 grade surface purity. The friction force of two bodies is known to be calculated as a sum of adhesive and deformation components [56]. For the case of rubber friction over the 14 grade surface purity metal the friction force is practically equal to the adhesive component, i.e. the observed decrease in the coefficient of starting friction in this case can be accounted for by the decrease in the adhesive interaction of fluorinated rubber with metal. Such explanation seems to be quite valid as the fluorinated layer formed on the rubber surface, according to its characteristics is similar to the perfluorinated polymers, which are characterized by high antiadhesive properties and low coefficients of friction [12, 57]. However, in such an approach a possible change in the area of actual contact of rubber with metal is not taken into account for fluorinated and nonfluorinated samples at the same normal load.

When a fluorinated rubber is in contact with the plates of stainless steel and duralumin with 9 and 10 grade surface purity a substantial decrease in the coefficient of starting friction is also observed. But these values are greater than the coefficients for Iogansen's plate, which seems to be associated with the occurrence of deformation component of the friction force, when the purity of indenter surface is decreased. In addition it should be mentioned, that the higher values of the coefficient of starting friction are observed during the contact of rubber with duralumin than during the contact with tool steel. The nature of indenter metal seems to show itself here; the adhesive interaction of rubber with duralumin surface is stronger than with the plate surface of stainless steel. Similar kinds of dependencies are obtained also for other elastomers.

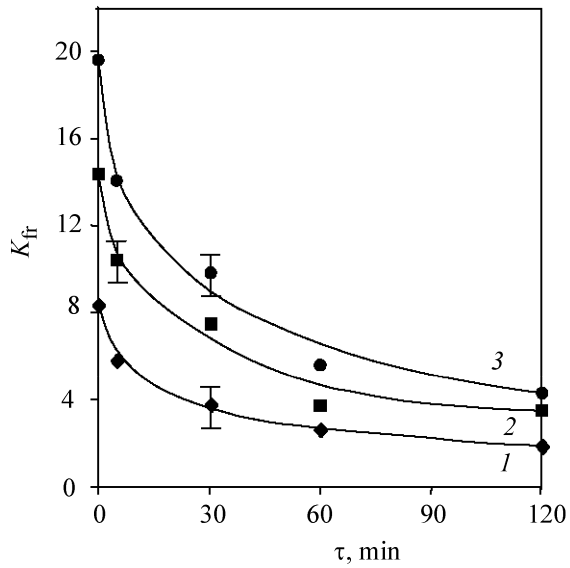

Fig. 13. The dependence of coefficient of starting friction on the duration of fluorination of SKN-26 samples for indenters of (*1*) Iogansen plates, (*2*) tool steel, and (*3*) type D16 duralumin.

The surface rubber fluorination results in an essential decrease in the coefficient of starting friction over metal, which is defined by a decrease in the adhesive interaction between the components. At the same time as the metal surface purity decreases, the deformation component of shearing force of the rubber relative to the metal surface increases, which can smooth the obtained effect at the expense of a decrease in the adhesive component of friction force.

Therefore, the presented results demonstrate a high efficiency of the method of surface fluorination of rubbers and also the possibility of its joint use with fluorine organic modifiers, which considerably improves tribotechnical characteristics of general mechanical rubber goods.

ACKNOWLEDGMENTS

The work is carried out with the financial help of RFFI (grant nos. 07-08-00109-a and 08-03-13513).

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