Elastomeric Composites Based on Frost-Resistant Rubbers Containing Karelian Deposit Natural Schungite

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Abstract. The article considers the problems of the operation of elastomers and elastomeric products in cold climates. It was shown that the combination of propylene oxide rubber (SKPO) and ultrafine polytetrafluoroethylene (UPTFE) was an effective way to obtain elastomeric materials with improved performance for operation in the northern regions. The general patterns of the influence of natural schungite on phase morphology and the properties of composites based on SKPO and UPTFE were investigated. It was found that with an introduction of small amounts of UPTFE (0.5-1 phr) the properties of elastomeric composites improve. It was associated with the structural features of the fluoropolymer. The particles of fluoropolymer had high activity, nanostructured organization, and the predominant concentration of fluoropolymer particles in surface layers of the material. The introduction of large quantities of UPTFE (50 phr) into the elastomeric matrix led to an improvement in the surface properties of the materials (wear and oil resistance). When substituting carbon black with natural schungite, both surface properties and physical and mechanical properties and compression set were improved. The obtained elastomeric composite will surpass many industrial elastomers by wear resistance and can ensure stable operation of seals under dynamic loading conditions (movable seals) and the presence of abrasives. Replacing carbon black in compositions based on SKPO and UPTFE with natural schungite will have a significant environmental and economic effect since it is much cheaper than carbon black.

1. Introduction
The Republic of Sakha (Yakutia) is a region characterized by extremely low temperatures (down to -60 °C) in winter, temperature differences with a large amplitude (up to 30 °C) in the autumn-spring period, high ultraviolet content due to the high transparency of the atmosphere and a large number of sunny days. These factors have a very adverse effect on elastomeric materials and products, which subjected to climatic ageing, lose elasticity due to lower ambient temperatures, freeze to metal surfaces and break when a force is applied [1]. Therefore, the elastomeric materials used in the northern regions should, first, have high frost and oil resistance, high level of strength, tribotechnical and relaxation properties. However, it is practically impossible to achieve a similar combination of properties in one material, since, for each of these properties, different factors are responsible which determine the structure and chemical composition of the elastomeric material. For example, low-temperature elasticity depends on the kinetic flexibility of the rubber chains, and resistance to the
effects of hydrocarbon media determined by the presence of polar groups in the carbon chain polymer that increase chain stiffness [2]. A combination of these properties can be obtained using the compositional principle by combining two or more polymers. In this case, it is necessary to correctly determine the nature of the mixed polymer components, their ratio, thermodynamic compatibility, the number and size of particles of active fillers and modifying additives that regulate the level of interfacial interaction and phase morphology of the composites.

Nowadays, propylene oxide rubber (SKPO), which is a copolymer of propylene oxide and allyl glycidyl ether, is a promising sealing material for Arctic applications. The presence of ether groups in the main chain gives the SKPO molecule great flexibility due to the low potential of the rotation barrier by the carbon-oxygen bond, which allows us to predict good low-temperature characteristics of the elastomer (glass transition temperature -74 °C). The polarity of the SKPO chain ensures higher oil resistance than elastomeric composites based on natural and isoprene rubbers. But SKPO based materials have lower oil resistance than elastomeric composites based on epichlorohydrin rubbers. The absence of unsaturated bonds in the main chain gives it greater resistance to the heat, oxygen, and ozone in comparison with unsaturated rubbers based on diene monomers [3, 4]. SKPO-based elastomeric composites proved to be excellent at full-scale tests in the climatic conditions of the Republic of Sakha (Yakutia) for 2 years. After exposure to the climatic conditions in oil, the frost resistance coefficient of the studied elastomeric composites remained stably high [5].

To meet the requirements for sealing elastomers for operation in the northern regions, SKPO was combined with ultrafine polytetrafluoroethylene (UPTFE). UPTFE (“Forum” dry lubricant, TU 2229-004-02698192-2002) has a low coefficient of friction, resistance to aggressive environments and high temperatures. The specific internal structure of UPTFE explains its increased adhesion, as well as its partial solubility in alcohol and acetone. These properties allow the components of polymer mixtures to better interact with each other at the phase boundary [6-10]. It is also of interest to introduce the Karelian deposit natural schungite as an active filler in this system to improve the properties and phase morphology of composites. It also allows reducing the cost of materials by replacing carbon black (CB) with natural raw materials, as well as increase the environmental friendliness of production.

Schungite is a natural polymorphic modification of carbon, which occupies an intermediate position between graphite, glassy carbon, and fullerenes [11,12]. The unique properties of schungite explained by its unusual internal structure. The carbon contained in schungite forms a matrix where dispersed silicates located evenly with the 1 μm average size. The mineral and carbon parts of schungite are not chemically bonded to each other. It can be introduced into almost all polar and nonpolar polymers, which is due to the presence of components with hydrophilic and hydrophobic properties and metastability of the structure of schungite carbon (SC) [12-16]. Researchers compare globular nanoscale SC formations in the form of layer structures with 0.35 nm between graphite-like planes that are transformed into polyhedral structures during heat treatment and grinding of schungite carbon [16].

Schungite due to its unique properties is widely used in rubber technology. It is used to improve the properties of elastomeric composites based on ethylene-propylene rubber [17,18], nitrile butadiene rubbers [19-21], chlorine-containing elastomers (polychloroprene, chlorosulfonated polyethylene, chlorobutyl rubber) [22], butadiene and isoprene copolymers [23]. Here it should be noted a significant contribution of researchers led by prof. Potapov E.E. They studied and popularized schungite as an environmentally friendly, cheap multifunctional filler of rubber compounds. The influence of schungite on the properties of rubbers was attributed by the researchers to its activity in the processes of restructuring elastomeric materials. In [24-29], the action of a schungite mineral activator during sulfuric vulcanization of styrene-butadiene and ethylene propylene diene rubbers was shown. Based on ideas about the role of the adsorption processes of accelerators and polymer units (butadiene and styrene) in the reactions of cross-linking of elastomers, it was confirmed that the surface of schungite is adsorption active for the components of the vulcanizing group. Using sulfur vulcanization of nitrile butadiene rubbers as an example, the possibility of replacing zinc oxide or most of it with schungite was shown [19]. Schungite has a cross-linking effect for systems based on
halogen-containing elastomers (polychloroprene, chlorobutyl rubber). The mechanisms of its interaction with these rubbers have been studied, which made it possible to remove ingredients partially or completely such as zinc oxide and magnesium oxide from rubber compositions [30, 31]. Besides, many researchers propose the use of schungite to replace the active rubber filler, carbon black, and it is possible to introduce schungite into rubber mixtures in large quantities (up to 50 phr) [17].

This mineral filler was never previously introduced into propylene oxide rubber. It would be interesting not only as an independent component of the mixture but also as an ingredient that improves interaction in complex heterogeneous systems based on mixtures of SKPO and UPTFE.

2. Materials and methods
UPTFE was added in small quantities from 0.5 to 10 phr in the first series of experiments in elastomeric composites based on SKPO. In the second series, UPTFE was introduced in large amounts from 20 to 50 phr. As the filler, we used carbon black P-803 or schungite. The filler was introduced into the composition in an amount of 60 phr. The complete replacement of filler with schungite in tested compositions eliminates the use of carbon black, which obtained from hydrocarbon raw materials. The use of schungite improves working conditions in production (schungite is less dusty) and reduces production costs.

We used schungite powder of the Zazhoginsky deposit (Karelia) with an average particle diameter up to 5 μm and a specific surface of 20 m²/g. Using X-ray analysis we identified (ARL X’TRA Thermo Fisher Scientific (Switzerland)) in the schungite of the Zazhoginsky deposit (Karelia), in addition to carbon, among the crystalline phase: quartz (SiO₂), pyrite (FeS₂) and a mineral of the mica group, most likely phlogopite.

The rubber blends were made in a Brabender PL 2200 plasticorder. The blend was vulcanized in an electric press at 150 °C. The compositions contained all the necessary ingredients of rubber compounds. The main operational characteristics of elastomeric composites were studied using standard methods: physical and mechanical properties by GOST 270-84, swelling degree by GOST 9.030-74, wear resistance by GOST 426-77, coefficient of frost resistance by elastic recovery by GOST 408-78, the abrasion resistance elastomeric composites of was studied using MI-2 friction machine and an AP-40 device. The structure was studied using a JSM-7800FX LV electron microscope (JEOL, Japan) equipped with an Oxford X-ray spectroscope.

The oil resistance of elastomeric composites with large amount schungite was determined according to GOST 9.030-74 in aviation oils MS-8P, MS-20, SM-4,5 and crude oil from the Irelyakhskoye field (IF). MS-20 oil (GOST 21743-76) - solvent extracted aviation oil, made from non-paraffin and paraffin oils with low sulfur content. It has a high viscosity, excellent adhesion, good lubricating properties and at least265 °C flashpoint. It used in piston engines of aircraft, in lubrication systems of turboprop engines. MS-8P (OST 38.101163-78) is the most widely used mineral oil with a complex of highly effective additives. The oil produced from West Siberian and a mixture of West Siberian and Ural oils. MS-8P intended for gas turbine engines of subsonic and supersonic aircraft the temperature of the oil leaving engine is not more than 150 °C. Oil MS-4,5 is a mixture of the first two oils in a ratio of 75:25 (mass fraction).

3. Results and discussion
3.1. SKPO-based elastomeric composites with a low content of UPTFE
As a result of the introduction of additives into the rubber blend, the following values of physical and mechanical properties were obtained (table 1):
Table 1. Physical and mechanical properties.

| Elastomeric composite | Tensile strength, MPa | Elongation at break, % | 100% modulus, MPa |
|-----------------------|-----------------------|------------------------|------------------|
|                       | CB        | schungite | CB        | schungite | CB        | schungite |
| SKPO initial          | 8,8       | 8,5       | 186       | 775       | 6,3       | 3,9       |
| SKPO +0,5 UPTFE       | 14,7      | 9,2       | 569       | 786       | 4,1       | 4,1       |
| SKPO +1 UPTFE         | 14,6      | 10,7      | 553       | 918       | 4,1       | 3,9       |
| SKPO +3 UPTFE         | 14,8      | 9,4       | 527       | 853       | 4,5       | 3,9       |
| SKPO +5 UPTFE         | 14,9      | 8,8       | 573       | 979       | 4,2       | 3,2       |
| SKPO +10 UPTFE        | 14,0      | 7,9       | 514       | 761       | 4,4       | 4,0       |

The analysis of the obtained physical and mechanical properties of elastomeric composites showed that the introduction of UPTFE powder over the entire considered concentration range in the blend based on SKPO (CB filler) leads to an increase in the values of tensile strength. In the entire considered range of UPTFE concentrations, the tensile strength increased by 30%, elongation at break by 3 times, and the modulus decreased by 35%. The introduction of UPTFE powder in small doses contributes to the development of highly elastic deformation. The rigidity of the system decreases with the addition of a fluoropolymer.

The physical and mechanical properties of elastomeric composites containing UPTFE with schungite indicate a small decrease of tensile strength compared with elastomeric composites containing CB but compared to the original composition with schungite tensile strength increased by 26%. The elongation at break of elastomeric composites increased almost 4 times after replacing CB with schungite, and when adding UPTFE powder, it increases by 26% for compositions containing 5 phr UPTFE (table 1). 100% modulus for elastomeric composites based on SKPO and UPTFE containing schungite is slightly lower compared to similar elastomeric composites filled with CB, i.e. they will deform at lower loads and exhibit highly elastic properties to a greater extent. Thus, schungite is not active filler as carbon black, but it leads to a significant improvement in the elasticity of the materials.

The introduction of UPTFE into the rubber blend with CB does not lead to significant changes in the compression set (Figure 1). With schungite the ability to elastic recovery of elastomeric composites increases to 16% (decrease of C). Blends containing small dosages from 0.5 to 1 phr UPTFE filled with schungite have the best compression set values.

![Figure 1. Dependence of the values of the compression set of elastomeric composites based on SKPO on the content of UPTFE: 1) CB filler, 2) schungite filler.](image-url)
Figure 2 shows the dependence of the volumetric wear values on the content of UPTFE in the composition. As the fluoropolymer content increases, the value decreased by 25% in blends with CB, and by 40% in blends with schungite. In previous studies, it was noted [32–35] that a similar effect upon the introduction of UPTFE into rubber blends filled with CB is associated with a partial redistribution of the fluorine-containing component between the surface and phase volume. The overall level of wear resistance of elastomeric composite filled with schungite is 14% higher than for elastomeric composite filled with CB.

![Figure 2. Dependence of the values of volumetric wear of elastomeric composites based on SKPO on the content of UPTFE: 1) filler CB, 2) schungite filler.](image)

Volumetric wear of elastomeric composites is predominantly a surface property. Frost resistance determined by the flexibility and mobility of the chains of macromolecules. As expected, the values of the coefficient of frost resistance of elastomeric composites at -20 °C and -50 °C with the introduction of fluoropolymer reduced. The average value of $K_M$ at -20 °C is 0.7, and $K_M$ at -50 °C is 0.3, which is quite acceptable for sealing elastomeric materials used in the Republic of Sakha (Yakutia), which is characterized by a sharply continental cold climate. Due to the presence of flexible ether bonds in the main chain, propylene oxide rubber characterized by unique frost resistance ($T_c = -72$ °C). The introduction of a hard fluorine-containing thermoplastic significantly reduces the coefficient of frost resistance, measured by the recovery of the material after compression. However, polytetrafluoroethylene is known as a material capable of operating at extremely low temperatures (down to -100 °C). It cannot repeatedly restore its shape after removal of deformation as elastomers, but we can expect that products from these materials will retain their integrity and performance at temperatures below -50 °C.  

3.2. **SKPO-based elastomeric composites with a high content of UPTFE**

In some cases, the main requirement for elastomers intended for use in cold climates is a high level of wear resistance. It is especially true for movable seals operating under dynamic loading conditions, for products operating under intense abrasive wear. Since UPTFE has a low coefficient of friction [6-10] and with its introduction, the tribotechnical characteristics of the obtained elastomeric composites will improve, in the next series of experiments, we decided to increase its content to 50 phr. Studies of elastomeric composites based on SKPO with a high content of UPTFE filled with carbon black showed that with an increase in the concentration of UPTFE from 20 to 50 phr there is a decrease in
the values of tensile strength, elongation at break (Figure 3) and coefficient of frost resistance both at -20 °C and -50 °C. This is associated with the inhibition of the development of highly elastic deformation in the presence of a high concentration of crystallized hard polymer at low temperatures.

The introduction of schungite positively affected the physical and mechanical properties of the elastomeric composites. The values of the tensile strength increased almost 2 times (Figure 3a), elongation at break increased 6 times (Figure 3b), 100% modulus decreased by an average of 17% (Figure 3c). I.e. it can be assumed that in the presence of schungite significantly changes the interaction of the initial polymer components of the mixture and another structure of the composition is created, providing a higher level of strength and highly elastic properties.

As in the case of compositions with low UPTFE content, the introduction of high concentrations of fluoropolymer leads to the improved wear resistance of elastomeric composites filled with CB. The difference in volumetric wear compared with the initial material depending on the content of UPTFE is from 2 to 21%.

Volumetric wear values also reduced in the case of compositions containing natural schungite (Figure 3d). The elastomeric composite based on SKPO, containing 50 phr of UPTFE and natural schungite as a filler has the best value of volumetric wear. The value is 25% better than the initial composition with a CB filler.

Studies to determine the ageing resistance during static compression deformation showed a similar positive trend. With the introduction of schungite, the compression set values are 23-30% lower than for elastomeric composites with the same amount of UPFE containing CB (Figure 4).
Figure 4. The dependence of the values of the compression set of elastomeric composites based on SKPO with different contents of UPTFE: 1 - CB filler, 2 - schungite filler.

For elastomeric composites containing high concentrations of UPTFE, the swelling degree in various aggressive hydrocarbons was additionally studied. For elastomeric composites containing a small amount of UPTFE (up to 10 phr), swelling degree values are not given, since the effect was insignificant. The study of oil resistance of elastomeric composites was carried out in the environment of MS-8P, MS-20, SM-4.5 aviation oils and crude oil from the Irelyakhskoye field. Oils are characterized by different physical and chemical compositions, which determines the differences in oil resistance of the studied elastomeric composites.

The swelling degree in all aggressive environments with the introduction of up to 50 phr UPTFE (CB filler) was reduced by 26-50%. The values were 8-13%, which is undoubtedly a positive result. UPTFE almost does not swell in hydrocarbon media, dilution of the elastomer with the medium oil resistance by this polymer (in this case, the amount of swelling material per unit volume reduced) leads to a significant decrease in the degree of swelling. The highest level of the swelling degree observed in MS-8P oil, low values of the swelling degree in MS-20 oil. MC-4.5 oil showed an intermediate position between MS-8P and MS-20 oils (Figure 4).

Figure 5. Swelling degree of elastomeric composites based on SKPO with different contents of UPTFE filled with TU in the medium of (1) crude oil from the Irelyakhskoye field (IF), oils (2) SM-4.5, (3) MS-20 and (4) MS-8P.
In the case of compositions containing natural schungite as a filler, the swelling degree was higher compared to filled with carbon black (from 18 to 60%), but with a content of UPTFE of 50 phr, the swelling degree was from 18 to 25%, which is also a positive result. In general, the values of the swelling degree correlate with the obtained values for elastomeric composites with CB; the lowest level of the swelling degree observed in the environment of MS-20 oil (Figure 5).

![Figure 6](image)

**Figure 6.** The swelling degree of elastomeric composites based on SKPO with different contents of UPTFE filled with schungite in the medium of (1) crude oil from the Irelakhskoye field (IF), oils (2) SM-4,5, (3) MS-20 and (4) MS-8P.

### 3.3. Study of phase morphology of UPTFE-highly filled elastomeric composites containing schungite

When large amounts of UPTFE (more than 10 phr) introduced into SKPO-based rubber blends (CB filler), the deformation and strength characteristics of the obtained elastomeric composites significantly decreased. The more fluorine-containing component, the more the tensile strength, modulus, compression set, and coefficient of frost resistance worsen. I.e. the bulk properties of the compositions deteriorated mainly due to the excess of the optimum degree of filling of the material corresponding to the uniform distribution of the second polymer component in the elastomeric matrix. However, properties such as oil resistance, wear resistance, i.e. those that are more superficial were significantly improved with the introduction of UPTFE. It is due to the unique surface and resistant properties of UPTFE. It is characterized by one of the lowest friction coefficients among existing polymers and is inert to most liquid media. The introduction of schungite in the composition instead of carbon black radically changed the situation. Some properties of these elastomeric composites, such as tensile strength, compression set practically do not concede to the characteristics of the initial elastomeric composite based on SKPO with increased wear and oil resistance. The elasticity of elastomeric composites based on SKPO and UPTFE containing schungite increased significantly. Such changes in properties can be explained by the features of the phase morphology of the mixed rubbers.

To study the structure of elastomeric composites using electron microscopy chips of the material were obtained by freezing in liquid nitrogen and cracking. The chips characterized the distribution of the fluorine-containing component in the volume of the elastomeric phase. The surface of the elastomeric composites was also studied. Therefore, it is of interest to compare the structural organization of the material in the volume and on the surface of elastomeric composite samples based on SKPO and UPTFE containing schungite. It will highlight the role of schungite in changing the properties of the resulting elastomeric composites.
Propylene oxide rubber forms a continuous phase with dispersed fluoropolymer particles. Microphotographs of the surface and volume of materials based on SKPO and UPTFE containing schungite (Fig. 7) indicate a different relief shape of materials and a change in the phase morphology of elastomeric composites. On microphotographs of the surface of the samples, structural formations about 10 μm in size were visible. With an increase in the content of UPTFE, structural elements were less pronounced. In micrographs of the volume, a change in morphology was also observed. At a content of 20 phr UPTFE structure is quite loose and developed, the relief is more pronounced, and at 50 phr fluoropolymer smoothing of the structural elements of the material was visible.

Figure 7. Micrographs of the surface and volume of samples based on SKPO + UPTFE (schungite filler) at x800 magnification.

The X-ray spectral studies showed that the elements contained in elastomeric composite, UPTFE and schungite (fluorine, zinc, silicon, aluminium, oxygen) were recorded in the volume and on the surface of the material. It was found that in the presence of schungite on the surface of elastomeric composites, the content of fluoropolymer particles is significantly lower than in the bulk of the material (Fig. 8, 9). In previous studies, it was found that with small amounts of UPTFE in CB-filled blends based on propylene oxide rubber [32–35] the fluorine content on the surface is higher than in volume. I.e. the surface of the samples was enriched with a fluorine-containing component due to different values of surface tension (σ) and surface energy of SKPO and UPTFE. The was a diffusion of the latter onto the surface during the preparation of compositions. According to the reference data [36], the value of σ calculated from the contact angle for PTFE is 19 mN / m, and for propylene oxide (the propylene oxide unit is the main structural unit of SKPO) is 32 mN / m. For these rubbers, an improvement was observed mainly in the surface properties of the material.
In the case of the introduction of significant amounts of UPTFE with schungite, we observed the opposite phenomenon. It can be assumed that the structure of the material based on mixtures of polymers was transformed in the presence of schungite. It is may be due to several phenomena: improving the interaction of fluoropolymer and propylene oxide rubber in the presence of schungite due to the adsorption of both polymer components on the surface of the filler having a diphilic nature, as well as improving the quality of mixing of polymer components in the preparation of the rubber blend due to the presence of fullerene and graphite-like structures in the composition of schungite. They act as solid lubricants in the preparation of the rubber compound. Both options are possible, since, for example, the possibility of adsorption of ethylene-propylene rubber on the surface of schungite in highly filled schungite mixtures was shown in [20] and the sizes of the interfacial layer having a sufficient extent were estimated. The unique composition of schungite, which has both a polar and non-polar component, can provide high affinity for both phases, for SKPO and UPTFE. In [17], a decrease in Mooney viscosity and an increase in the plasticity of compounds during mixing observed. One of the explanations is the presence of fullerene-like structures in the composition.

Figure 8. Electron micrographs of elastomeric composite based on SKPO with a content of 50 phr UPTFE (schungite filler) chipped in liquid nitrogen sample and distribution maps of Si and F elements (800x magnification).

Figure 9. Electron micrographs of the elastomeric composite based on SKPO with a content of 50 phr UPTFE (schungite filler) sample surface and distribution maps of Si and F elements (800x magnification).
4. Conclusions

Our previous studies showed that with the introduction of small doses of UPTFE (0.5-1 phr) in rubber blends filled with CB, the properties of elastomeric composites improve. It was associated with the structural features of the ultrafine fluoropolymer, namely, the high activity of its particles, their nanostructured organization, better uniformity of distribution in the volume of the elastomeric matrix, good dispersion in the mixture and transformation of the structure of the propylene oxide matrix in the presence of ultrafine particles of the fluoropolymer. The increase in the content of UPTFE to 50 phr in the composition led to a decrease in strength and elasticity, frost resistance, and compression set, but increased oil resistance and wear resistance of the elastomeric composite. The material works stably under abrasive wear.

Replacing carbon black with natural schungite in rubber blends of a similar composition based on SKPO and UPTFE led to a noticeable increase in physical and mechanical properties and a decrease in the compression set. In this case, the volumetric wear of elastomeric composites was reduced by 19%, and the degree of swelling up to 30%. The reason for improving the properties with the schungite may be due to the chemical composition. Schungite contains both organic (nanosized carbon, fullerenes) and inorganic components (metal oxides, silicon oxide), which provide interaction with oxygen-containing propylene oxide rubber.

The optimal composition of elastomeric composites for use as sealing parts in the North in conditions of abrasive wear is the propylene oxide rubber-based material containing 50 phr of ultrafine polytetrafluoroethylene. We recommend using natural schungite as an active filler instead of CB. Due to the low coefficient of friction, which is practically independent of sliding speed, these elastomeric composites will surpass many industrial elastomers in terms of wear resistance. The material can ensure stable operation of seals under dynamic loading conditions (moving seals) and the presence of abrasives. The high cost of UPTFE is likely to prevent the use of these materials, but for severe operating conditions they will be useful. Besides, the introduction of schungite as an active filler reduces the cost of the product by replacing expensive carbon black with natural mineral raw materials and will increase the environmental friendliness of products. All this allows us to recommend the developed elastomeric composite for use in cold climates to produce elastomeric sealing parts operating in conditions of intense abrasive wear.

5. References

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