Elastomeric composites for Arctic conditions: operation features and development experience

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Abstract. Operation of elastomeric materials in the extreme climatic conditions of the North is complex and expensive, since not always existing materials can provide the required level of low-temperature characteristics (down to - 60 °C). This leads to failure of machines and mechanisms, equipment downtime, additional costs for repair or replacement of elastomeric parts. This study investigates the features of elastomeric composites operation in cold climates and the results of full-scale tests with simultaneous exposure to naturally low temperatures and hydrocarbon environments in Yakutia (Siberia, Russia). It presents the main principles of creating elastomeric composites for sealing purposes with high frost resistance and examples of recent developments. To obtain elastomeric materials of high frost and oil resistance new rubbers of high frost resistance as Hydrin T6000 epichlorohydrin rubber ($T_f = - 60$ °C), and traditional rubbers (nitrile etc) were used. For elastomer modification we used carbon nanotubes, collagen hydrolysate and polymer mixtures. Different type of developed materials is a double-layer material based on ultra-high-molecular-weight polyethylene (UHMWPE) and nitrile-butadiene rubber-based elastomeric composite. The effect of diphenylguanidine on the interaction of UHMWPE with elastomeric composite based on nitrile butadiene rubber and adhesion at the interface was investigated. The operating properties were studied by standard methods and the structure of the obtained materials was studied using electron microscopy.

1. Introduction

Elastomers are the class of polymers with a peculiar set of properties that differ from most of the known thermoplastics, thermosetting plastics, or polymer fibres. They characterized by high elasticity, i.e. the ability to undergo significant (up to a thousand per cent or more) reversible deformations at low values of stresses, low modulus combined with mechanical strength and performance over a wide temperature range [1]. As a result, elastomer materials (elastomeric composites) are unsurpassed materials for sealing purposes. They are applied widely to produce various types of seals, gaskets, cuffs, damping products. Machines and mechanisms are completed with these products. They also used as functional sealing parts, sealing joints and joints of parts of technological equipment, as part of friction units. The
The performance of the entire unit or the mechanism largely depends on the properties of elastomeric seals and their ability to seal joints.

Sealing purpose elastomeric materials must have several properties, including a certain level of physical and mechanical characteristics (products must withstand operating pressures and loads), resistance in working environments, most often of a hydrocarbon nature (oil, fuel), frost resistance required for operation in various climatic zones, the ability of products to restore their shape during operation, which is most often assessed by compression set, a certain level of wear resistance. All these properties are different and are the result of the various processes in an elastomeric composite. So, frost resistance determined by the flexibility and mobility of macromolecular chains of rubber, characterized by the degree of development of highly elastic deformation at the operating temperature. Its lower limit of manifestation is the glass transition temperature \( T_g \), which determines the transition of an elastomeric material from a glassy state to a highly elastic state of relaxation nature. Compression set is also a consequence of the manifestation of the relaxation properties of the material. The resistance of rubbers in hydrocarbon media is determined by the presence of polar fragments in the elastomer structure, which, however, reduce the flexibility and mobility of macromolecules, i.e. reduce the frost resistance of the material. Tensile strength and wear resistance are complex indicators that characterize both the structure and mechanical properties of the material, and the presence of various defects. The entire volume of the sample makes a greater contribution to the manifestation of physical and mechanical properties. The structure and composition of the surface layers of the material makes the greatest contribution to the wear resistance of rubbers. Thus, when developing elastomeric composites for sealing purposes, it is necessary to provide an optimal combination of all these characteristics, which, of course, is not an easy task. This combination of various properties in one material should ensure long-term operation of products made of elastomeric materials, minimal leakage of working fluids, and trouble-free operation in real conditions.

Many works devoted to the study of the operation of elastomeric seals at low temperatures [2-6]. There are works studying an interfacial leakage of O-rings in sealing joints [2,3], and factors influencing low temperature flexibility of elastomers [4]. However, the properties of the seals are considered down to -25\(^\circ\)C to -30\(^\circ\)C. In general, lower winter operating temperatures not realized in European countries. Still, further advancement into the Arctic (offshore oil and other minerals production) makes the development of elastomeric materials of unique frost resistance urgent. This article is devoted to this subject.

When an elastomeric composite operated in cold climates, for example, in the Arctic zone of the Russian Federation (Republic of Sakha (Yakutia)), the requirements for materials become more stringent, especially in terms of frost resistance. The climate of Yakutia is characterized by extremely low temperatures (up to -60\(^\circ\)C) in winter, their frequent changes with a transition through 0\(^\circ\)C with an amplitude of up to 30\(^\circ\)C to 40\(^\circ\)C in the autumn-spring period, high content of ultraviolet radiation due to the high transparency of the atmosphere and a large number of sunny days. All this leads to the fact that traditional industrial rubbers do not correspond to the operating conditions, due to rapid ageing and low temperatures, they become hard, not elastic, which leads to a decrease in the tightness of the connection, leaks of the working medium, and destruction of sealing parts. As the practice of operating machines and mechanisms in the Republic of Sakha (Yakutia) has shown, up to 30% of the total number of equipment failures in winter is caused by insufficient frost resistance of elastomeric products, which leads to equipment downtime, the need for repair work, and can initiate disasters and negative consequences for the environment [7].

We have carried out comprehensive tests of industrial elastomeric materials based on nitrile butadiene, propylene oxide, epichlorohydrin rubbers under the conditions of natural exposure of samples in the climatic conditions of Yakutia in a hydrocarbon environment (oil) [8-10]. Nitrile butadiene rubber with a low content of acrylonitrile (BNKS-18, \( T_g = 50 \, ^\circ\)C) is of limited use under these conditions. As a rule, significant amounts of plasticizers - substances that improve the flexibility and mobility of rubber macromolecules - are introduced into industrial elastomeric composites based on BNKS-18. However, this method of increasing frost resistance turns out to be ineffective for elastomeric composites in contact
with carbon media during operation because plasticizers are quickly washed out by the medium. Elastomeric composites based on rubbers of high frost resistance, for example, propylene oxide (Russia, \(T_g = -74\, ^\circ\text{C}\)) or epichlorohydrin rubber Hydrin T6000 (Japan, Zeon, \(T_g = -60\, ^\circ\text{C}\)) have excellent prospects for operation in extreme conditions of the Arctic [11].

Over the years, we have developed basic approaches to creating elastomeric composites that combine an increased level of frost and oil resistance [12]. They are systematized in the diagram shown in figure 1. There are two main ways to obtain such materials: using one rubber or a mixture of polymers to achieve a compromise combination of basic properties. In the first case, it is necessary to use mainly rubbers of high frost resistance as a basis; if BNKS-18 is used, then measures should be taken to slow down the washout of the plasticizers. In the second case, we are talking about the creation of composite materials based on mixtures of polymers with a certain phase morphology and increased interaction of rubbers at the interface, and in the extreme case, their co-vulcanization. If in either case the achieved level of oil resistance of materials while maintaining frost resistance is insufficient, then a surface modification of the elastomers should be carried out to protect the surface from the effects of environments. At the same time, for the reliable operation of products, it is important to securely attach the coating to the substrate, \textit{i.e.} ensuring increased adhesion at the border of their contact.

![Figure 1. Ways to create materials with a high level of frost and oil resistance.](image)

The proposed principles of creating frost-resistant materials have been tested and have shown their effectiveness. We have developed several elastomeric composites of various compositions, for which patents of the Russian Federation and the USA have been obtained. In this study, some recent developments are presented that confirm the correctness of the proposed scheme. In the first case, elastomeric composites based on epichlorohydrin rubber Hydrin T6000, modified with carbon nanotubes or a specially obtained environmentally friendly additive of a collagen nature, are considered.
Blends based on mixtures of diene and nitrile butadiene rubbers are considered as an example of the use of the compositional principle to produce elastomeric materials for Arctic use. In conclusion, a method for producing two-layer materials based on nitrile butadiene rubber and ultra-high molecular weight polyethylene is presented.

2. Materials and methods
The following rubbers were used in this work: Hydrin T6000 epichlorohydrin rubber, a terpolymer of epichlorohydrin, propylene oxide and allyl glycidyl ether (GPCO) [13]; nitrile-butadiene rubber (NBR), a copolymer of butadiene and nitrile of acrylic acid (BNKS-18, BNKS-26); and also butadiene (SKD) and isoprene (SKI-3) rubbers. Nitrile-butadiene rubbers are one of the most common rubbers to produce elastomeric composites for sealing purposes. They have a balanced set of properties, BNKS-18 combines frost resistance ($T_g = - 50 ^\circ C$) and oil resistance, but both properties need to be improved. Hydrin T6000 has high frost resistance ($T_g = - 60 ^\circ C$), oil resistance at the level of BNKS-18, but the property usually needs to be increased [14]. The vulcanizates of Hydrin T6000 has low wear resistance. GPCO epichlorohydrin and BNKS nitrile rubbers were used as the basis for the individual rubber elastomeric composite. Subsequently, they were modified with carbon nanotubes and collagen hydrolysate.

The properties of elastomeric composites based on rubber mixtures can be not only additive but also exceed the properties predicted by the ratio of rubbers in the mixture. This is also true in relation to frost resistance. When ingredients are introduced into a mixture of rubbers, the structure and properties of the obtained elastomeric composites can change significantly, which makes it possible to create materials with the required level of properties. Nitrile butadiene rubbers BNKS-18 and BNKS-26 were chosen as components of the mixture responsible for resistance to aggressive working environments, and diene rubbers were chosen as components responsible for frost resistance and wear resistance: butadiene (SKD) and isoprene (SKI-3) rubbers. SKD has a low glass transition temperature ($T_g = -100 ^\circ C$) but it is a highly crystallizing rubber, which significantly reduces its long-term frost resistance. Due to thermodynamic incompatibility, elastomeric composites based on mixtures of the two rubbers have two glass transition temperatures, respectively. For crystallizable rubbers, the addition of the second component can slow down the crystallization rate. A typical example of such system is a mixture of SKI-3 isoprene rubber with SKD butadiene rubber, where SKI-3 suppresses the crystallization rate of SKD [15]. Low-temperature performance of the elastomers based on this mixture is better than elastomers based on individual SKD and SKI-3 rubbers due to lower crystallization rate. When combined with nitrile rubbers, the resulting structure can impede the crystallization of diene rubbers at low temperatures.

Multi-walled carbon nanotubes (MWCNTs) manufactured by the Research Center for Radiation Application (China) were used as a carbon nanofiller for Hydrin T6000. These nanofillers were chosen after preliminary investigation of the effect of nanotubes of various compositions: functionalized (MWCNT) and not functionalized with oxygen groups (single-walled CNTs manufactured by OSiAl, Russia).

To determine the optimal content of the nanofiller, we studied rubber blends containing from 0.05 to 10 phr (parts per hundred parts of rubber) MWCNTs. Carbon nanotubes are one of the promising nanofillers that used in many types of elastomeric composites. However, MWCNTs was not previously used to modify GPCO epichlorohydrin rubber. The elastomeric composites were prepared using traditional technology. The developed elastomeric material contained all the necessary ingredients: dispersants, vulcanization activators and accelerators, antioxidant, 50 phr (parts per hundred parts of rubber) of P803 carbon black, sulphur as vulcanization agent. The blends additionally contained from 0.1 up to phr of MWCNTs. The mixtures were prepared in a standard way in a closed “Brabender” plasticorder at 50 °C with 40 rpm shaft rotation speed in 15 minutes, then vulcanized in a vulcanization press.

Hydrin T6000 epichlorohydrin rubber, as well as BNKS-18, BNKS-26 containing 18, 26 % by weight of acrylonitrile respectively, were also modified with collagen hydrolysate obtained from the
swim bladder of northern fish, which considered as a multifunctional environmentally friendly modifier. Collagen hydrolysate was obtained from the swim bladder of northern species of fish with alkali-salt hydrolysis followed by freeze-drying. Collagen hydrolysate was added in a quantity of 1, 2, 3, 4, 5 phr with sulphur vulcanization system.

The rubber blends were prepared in a Brabender plasticorder, they contained all the necessary ingredients (accelerators and activators of vulcanization, sulphur, an active filler - carbon black, etc.), then they were Vulcanized in an electric press.

To obtain double-layer materials a substrate based on BNKS-18 was used, on which a coating of ultra-high-molecular-weight polyethylene (UHMWPE) was applied. UHMWPE has high physical and mechanical properties, practically does not wear out. A high degree of polymer crystallinity determines its low degree of swelling in hydrocarbon media. We also studied the effect of diphenylguanidine (DPG) on the adhesive interaction between GUR-4113 grade UHMWPE with an average molecular weight of 3.9 million g / mol and elastomeric composite based on nitrile butadiene rubber. The technological process of manufacturing products from UHMWPE and elastomeric composite is carried out by hot pressing. It is known [16,17] that the processing temperatures of elastomers and UHMWPE are in the same temperature range from 145 °C to 180 °C, which made it possible to develop a technology for applying it to the surface of an elastomeric material.

The kinetics of vulcanization was studied on a Monsanto rheometer (GOST 12535-84) to identify the effect of modifying additives (MWCNT, collagen hydrolysate) on the properties of Hydrin T6000 and BNKS based elastomeric materials. The kinetic parameters of the crosslinking process of rubber compounds were determined, such as the optimum vulcanization and the rate of crosslinking of vulcanizates.

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, compression set by GOST 9.029-74, wear resistance by GOST 426-77. The abrasion resistance elastomeric composites were studied using MI-2 friction machine and an AP-40 device. The structure of materials was investigated using a JSM-7800FX LV electron microscope (JEOL, Japan) equipped with an Oxford X-ray spectroscopy.

The study of the strength of the adhesive bond between elastomers and UHMWPE was carried out by GOST 6768-75 on a Shimadzu Autograph tensile testing machine (Shimadzu, Japan). Investigation of the structure of the interphase boundary layer of the elastomer and UHMWPE was carried out on a JEOL JSM-7800F scanning electron microscope.

3. Results and discussion

3.1. Epichlorohydrin rubber based elastomeric composites modified with carbon nanotubes

Problems associated with improving the properties of elastomeric composites can be solved in various ways. Most often by changing the composition of rubber blend. To achieve the desired level of the properties of elastomeric composites based on Hydrin T6000 epichlorohydrin rubber we used carbon MWCNTs.

Electron microscopic studies of MWCNTs (figure 2) showed that MWCNTs were agglomerated with a fine structure in the form of nanofibers with a diameter of 20-47 nm and a length of 8-30 μm. The surface of carbon nanotubes was investigated using an X-max20 energy-dispersive attachment from OXFORD. It was found that in addition to carbon (88% by weight), it also contains up to 10% oxygen (figure 3). Functionalization of multi-walled carbon nanotubes with oxygen gives a definite advantage over analogues because oxygen atoms are also present in the main chain of GPCO epichlorohydrin rubbers. It should contribute to the uniform distribution of MWCNTs in the bulk of the rubber blend at the mixing stage. The presence of Co and Al elements is explained by the residues of the catalytic system used in the synthesis of nanotubes.
The analysis of the rheometric curves showed that the introduction of MWCNTs does not significantly affect the technological parameters: the viscosity of modified rubbers, the crosslinking rate and the optimum vulcanization do not undergo significant changes.

**Figure 2.** Electron micrographs of MWCNTs.

| Element | Mass %  | Atomic % |
|---------|---------|----------|
| C       | 88.34   | 91.73    |
| O       | 9.89    | 7.71     |
| Al      | 0.76    | 0.35     |
| Co      | 1.01    | 0.21     |

**Figure 3.** Elemental composition of MWCNTs.

Table 1 shows the properties of Hydrin T6000 epichlorohydrin rubber based elastomeric composites modified with nanotubes.

**Table 1.** Properties of elastomeric composites based on epichlorohydrin rubber modified with MWCNTs

| Hydrin T6000+ MWCNTs phr | ε_p (%) | f_p (MPa) | f_{100} (%) | C^d (%) | ΔQ^e (%) | ΔV^f (cm³) |
|---------------------------|---------|-----------|-------------|---------|----------|------------|
| GPCO                      | 364     | 11.0      | 3.6         | 61.2    | 35.5     | 1.30       |
| GPCO / 0.05               | 346     | 10.0      | 3.2         | 63.2    | 34.8     | 0.90       |
| GPCO / 0,1                | 368     | 10.8      | 3.2         | 62.2    | 35.2     | 0.87       |
| GPCO / 0,2                | 339     | 10.8      | 3.3         | 61.2    | 36.6     | 0.92       |
| GPCO / 0,3                | 339     | 11.0      | 3.2         | 63.0    | 35.0     | 0.84       |
| GPCO / 0,5                | 339     | 11.0      | 3.9         | 61.2    | 33.3     | 0.76       |
| GPCO / 1                  | 328     | 11.0      | 3.3         | 59.5    | 32.7     | 0.78       |
| GPCO / 2                  | 312     | 11.0      | 4.6         | 64.0    | 20.1     | 0.75       |
| GPCO / 5                  | 229     | 11.0      | 5.7         | 67.1    | 21.2     | 0.72       |
| GPCO / 10                 | 183     | 12.0      | 8.0         | 69.3    | 17.3     | 0.69       |

\(^a\) elongation at break.  
\(^b\) tensile strength.  
\(^c\) 100% modulus.  
\(^d\) compression set at 100 °C and 72 h.  
\(^e\) swelling degree at 70 °C and 72 h in oil.  
\(^f\) volumetric wear.
Our study of physical and mechanical properties showed that as the content of MWCNTs increased, the strength characteristics of elastomeric composites based on Hydrin T6000 GPCO tend to increase. However, at high concentrations of MWCNTs, the elongation decreased significantly (by 49%), and the modulus doubled. It was found that the introduction of MWCNTs had the strongest effect on the wear resistance and the degree of swelling. Thus, the volumetric wear of the obtained elastomeric composites with an increase in the concentration of nanotubes decreased to 47%, which was apparently associated with a decrease in the values of the statistical and dynamic coefficients of friction of elastomeric composites based on Hydrin T6000 GPCO modified with MWCNTs [18]. The degree of swelling at high contents of MWCNTs was also reduced two times.

Among all considered contents of nanotubes, the optimum properties were observed with the introduction of 1 phr of MWCNTs. These elastomeric composites, as was shown using electron microscopy, were characterized by the most uniform distribution of MWCNTs in the elastomeric matrix, high wear resistance (by 40%), lower compression set and the degree of swelling compared to the initial unfilled elastomeric composite, while maintaining high elasticity and strength characteristics.

3.2. Epichlorohydrin rubber based elastomeric composites modified with collagen hydrolysate

Recently there has been a development in the manufacturing of new biodegradable polymeric materials. The introduction of biologically active compounds such as keratin, lignin, starch, amino acids, and phospholipids into the polymer matrix allows obtaining elastomeric composites with improved properties. In this work, we obtained a collagen hydrolysate from the swimming bladder of northern species of fish. It was used as a modifier of elastomeric compounds such as Hydrin T6000 GPCO epichlorohydrin rubber, nitrile-butadiene–rubbers (BNKS-18, BNKS-26). Collagen hydrolysate was obtained from the swim bladder of northern species of fish with alkali-salt hydrolysis followed by freeze-drying. The substance retained its collagen nature and a set of functional groups inherent in proteins during hydrolysis. Collagen hydrolysate was added in a quantity of 1, 2, 3, 4, 5 phr with sulphur vulcanization system. Its effect was investigated on model non-carbon black filled blends based on BNKS-18, BNKS-26.

It was found that collagen hydrolysate affects the structuring process of the studied rubbers. The data of vulcanization kinetics showed that the introduction of the collagen hydrolysate into the rubber compound had a significant effect on the duration of their cure time and the cure rate index. Comparing results of the cure rate index for the control samples and the modified samples, showed that the cure rate index increases with the introduction of a collagen hydrolysate by 216%, 359%, 83% based on BNKS-18, BNKS-26 and Hydrin T6000 GPCO, respectively. Moreover, a collagen hydrolysate reduced the cure time vulcanization. It can be assumed that the collagen hydrolysate was involved in the crosslinking of the elastomeric material, contributing to the formation of additional cross-links between the macromolecules.

The qualitative analysis of the IR spectroscopy data indicated new absorption bands appear in the spectra of NBR compounds containing hydrolysate. The presence of a new absorption band at 1562 cm⁻¹ which corresponds vibrations of NH–, C = N– bonds of collagen, may indicate a chemical interaction of the studied rubbers with hydrolysate. Table 2 presents the results of the effect collagen hydrolysate on mechanical properties of blends.

The study of physical and mechanical properties showed that the addition of the collagen hydrolysate promoted an increase in tensile strength of the NBR rubber. It was explained by the cross-link density increase of rubber with the introduction of collagen [19]. It should be noted that all blends of NBR rubber filled with collagen hydrolysate were characterized by a higher cross-linking density compared with control samples which did not contain hydrolysate.

At the same time, the modifier did not cause a significant effect on the physical and mechanical properties of Hydrin T6000 GPCO blends. The tensile strength of the Hydrin T6000 GPCO filled with collagen hydrolysate remained almost at the level of the control samples. It was found that the use of collagen hydrolysate as a filler of blends caused a reduction of the level of compression set accumulation of elastomeric composites based on GPCO and NBR. The compression set of NBR and GPCO were
decreased with increasing collagen hydrolysate content in blends. The compression set decreased by 27% and 20% compared with the control samples based on NBR, GPCO, respectively.

It can be assumed that the collagen hydrolysate may be a secondary curing agent. To verify that the collagen was involved in cross-linking processes, the structures of blends were investigated using electron microscopy. Scanning electron microscopy was used to observe the morphology of the control samples of NBR and blends filled only collagen hydrolysate. These blends were prepared in Brabender plasticorder and subjected to heating in an electric press at a vulcanization temperature at the same conditions as described above but did not contain the sulphur vulcanization systems. The images are shown in figure 4.

![Figure 4. SEM images of blends (150°):](image)

|          | 1 – NBR-18, (150°) | 2 – NBR-18, filled 1 phr. collagen hydrolysate | 3 – NBR-18, filled 3 phr. collagen hydrolysate; (5000°) |
|----------|--------------------|-----------------------------------------------|-------------------------------------------------------|
| 4 – NBR-18, (5000°) | NBR-18, filled 3 phr. collagen hydrolysate | NBR-18, 3 phr. collagen hydrolysate              |

Table 2. Properties of elastomeric composites based on epichlorohydrin rubber modified with MWCNTs

| Collagen hydrolysate, phr | BNKS-18 | BNKS-26 | Hydrin T6000 GPCO |
|---------------------------|---------|---------|------------------|
|                           | $f_p$ (MPa) | $C$ (%) | $\nu_c$ (mol/cm$^3$) | $f_p$ (MPa) | $C$ (%) | $\nu_c$ (mol/cm$^3$) | $f_p$ (MPa) | $C$ (%) | $\nu_c$ (mol/cm$^3$) |
| 0                         | 3.5     | 80      | 0.96             | 5.3      | 80      | 1.26             | 7.6      | 65      | 3.5              |
| 1                         | 3.2     | 70      | 1.39             | 4.2      | 66      | 1.37             | 8.2      | 64      | 3.2              |
| 2                         | 3.8     | 66      | 1.53             | 4.1      | 66      | 1.72             | 7.6      | 60      | 3.8              |
| 3                         | 4.5     | 68      | 1.57             | 4.6      | 63      | 1.50             | 7.9      | 57      | 4.5              |
| 4                         | 4.7     | 68      | 1.55             | 3.5      | 76      | 1.28             | 6.9      | 53      | 4.7              |
| 5                         | 5.2     | 66      | 1.24             | -        | -       | -                | 7.0      | 61      | 5.2              |

$^a$ tensile strength.

$^b$ compression set at 100 °C and 72 h.

$^c$ crosslink density
The surface of elastomeric composite containing collagen was embossed, which can indicate that the collagen hydrolysate could be involved in the formation of new cross-links with the rubber macromolecule. This explained with the introduction of hydrolysate in the rubber formulation, the density of the network increases (table 2), which may be a consequence of additional crosslinking of rubber macromolecules. Crosslink density of compounds was determined by the solvent swelling method using the Flory–Rehner equation. For this purpose, the insoluble blends gel remaining after extraction was dried to constant weight, and then it was subjected to swelling in chloroform at room temperature for 18 h.

The introduction of small amounts of collagen hydrolysate into rubber blends led to a significant increase in the cure rate index, a reduction of the level of compression set accumulation while increasing or maintaining the mechanical properties of the modified rubbers, which is associated with the chemical modification of elastomers by collagen hydrolysate and an increase in the density of the network of vulcanization bonds. Thus, the collagen hydrolysate obtained from swim bladder is a new promising rubber compound modifier.

3.3. Elastomeric composites based on mixtures of diene and nitrile butadiene rubbers

The ratio between nitrile butadiene (BNKS-18, BNKS-26) and diene rubbers (SKD, SKI-3) was 70:30. The nitrile-butadiene phase prevailed to provide acceptable aggressive media resistance in non-polar hydrocarbon mineral environments. Stability in synthetic polar media was provided by diene rubbers.

The composition of elastomeric composites also included: vulcanization activators, vulcanization accelerators, antioxidant, carbon black filler, plasticizer, vulcanizing agent. The rubber blend was obtained based on nitrile butadiene rubbers BNKS-18 and BNKS-26, into which 40% of the total carbon black and the plasticizer were added, which is then combined with the diene rubbers and the remaining ingredients (figure 5).

![Figure 5. Elastomeric composites mixing technology based on mixture of rubbers](image)

| Table 3. Properties of elastomeric composites based on mixture of rubbers |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Hydrin T600+ MWCNTs phr | $e_p$ (%) | $f_p$ (MPa) | $f_{100}$ (MPa) | $C_1$ (%) | $\Delta Q$ (%) | $T_g$ (°C) | $\Delta V$ (cm³) |
| V-14 | 223 | 9.0 | 5.1 | 74.0 | 2.19 | -45.3 | 1.297 |
| NBR+diene | 428.1 | 10.0 | 2.2 | 66.2 | 18.6 | -60.2 | 0.697 |

$^a$ elongation at break.
$^b$ tensile strength.
$^c$ 100% modulus.
$^d$ compression set at 100 °C and 72 h.
$^e$ swelling degree at 70 °C and 72 h in hydraulic oil.
$^f$ glass transition temperature.
$^g$ volumetric wear.

This method of combining provides better mixing due to a different ratio of the viscosities of the diene and nitrile rubber phases and a more uniform distribution of the components in the mixture. After
mixing the rubber blend in the Brabender plasticorder it was cured in an electric hydraulic press. The obtained properties are shown in Table 3.

For comparison, the characteristics of industrial rubber V-14, based on rubber BNKS-18, are given. Tensile strength of the investigated elastomeric composite based of rubber mixture was comparable to the V-14 rubber. The elasticity of the investigated elastomeric composite was 1.9 times higher than V-14. The compression set values for the investigated elastomeric composite were 8% lower than that of V-14. Lower values of the compression set indicate better relaxation properties of the material (better recoverability after unloading after accelerated ageing), which are an important indicator for elastomeric composite for sealing purposes. The elastomeric composite based of rubber mixture had increased wear resistance: volumetric wear was 1.9 times lower than for V-14 rubber. The glass transition temperature was -60.2 °C. The value is 14.9 °C lower than that of V-14 rubber. It should also be noted that the high frost resistance of the elastomeric composite based on mixtures of butadiene-nitride and diene rubbers was due not to the presence of plasticizers, but the polymer base having high low-temperature characteristics. This elastomeric composite based on mixture of rubbers was patented (RU 2 705 069 C1).

3.4. Effect of diphenylguanidine on the adhesive interaction of ultra-high molecular weight polyethylene and elastomeric composite based on nitrile butadiene rubber

Currently, polymer composite materials are increasingly finding widespread use in various industries due to their unique qualities and relatively simple processing process. Polymer products are used as structural and functional materials in critical units and joints in mechanical engineering, automotive and aircraft construction [20,21]. Elastomeric materials remain unsurpassed sealing materials, but their seals perform at lower loads and sliding speeds than other polymer classes. In this regard, there is a constant search and development of new polymeric materials, which are subject to even higher reliability requirements during operation. One of the most effective methods for manufacturing materials with improved performance is the application of thermoplastic coatings on elastomeric materials or the creation of multilayer polymeric materials. The advantage of the method is the ability to combine the properties of different materials in one product - rigidity, elasticity, hardness, and damping properties. One of the possible ways of creating a double-layer material is a combination of thermosetting plastic with a thermoplastic. It can be elastomer and polyethylene as shown in Figure 6. These materials are thermodynamically incompatible, i.e. adhesion at the contact boundary is low. It is necessary to take several measures to increase the reliability of the operation of such materials.

![Figure 6. Double-layer material based on UHMWPE and rubber.](image)

We investigated the effect of DPG, an accelerator of sulphur vulcanization of medium activity, on the adhesive interaction between GUR-4113 UHMWPE and elastomeric composite based on nitrile butadiene rubber (BNKS-18). DPG used as secondary accelerators in combination with higher activity primary accelerators. As it was found in [22], the addition of DPG with sulphur to polyethylene leads to the formation of sulphide bonds between polyethylene macromolecules. Since UHMWPE is also polyethylene by chemical structure, the same chemical processes of interaction with sulphur apply to it.

We have developed a technology for producing double-layer materials, based on joint hot pressing at a temperature of 155 °C, which creates conditions for good interaction of the components. The study of the strength of the adhesive bond between elastomers and UHMWPE was carried out by analogy with GOST 6768-75 on a Shimadzu Autograph tensile machine. Investigation of the structure of the interphase boundary layer of the elastomer and UHMWPE was carried out on the scanning electron
microscope. Table 4 shows the results of a study of the effect of adding 0.3 phr of DPG in the process of mixing the rubber blend ingredients to adhesion between the elastomer and UHMWPE.

Table 4. Adhesion of UHMWPE with an elastomer based on NBR

| Sample                  | Adhesion, N/cm |
|-------------------------|----------------|
| UHMWPE / NBR            | 56             |
| UHMWPE / NBR + 0.3 DPG  | 148            |

In the process of delamination of double-layer samples based on BNKS-18 rubber with DPG, destruction occurred on the elastomer. This indicates that the adhesive interaction between materials exceeded the cohesive strength of rubber. When a double-layer material without DPG was delaminated, destruction occurs along the contact boundary.

The introduction of DPG into the rubber blend led to an increase in the intensity of crosslinking of rubber macromolecules with UHMWPE (covulcanization) and a change in the supramolecular structure, which can be seen in micrographs of the interaction interface (Figure 7, b). The process of formation of an adhesive bond between UHMWPE and elastomer occurs according to different mechanisms, depending on the ingredients introduced into the rubber mixture.

![Figure 7. Micrographs of UHMWPE transitional layer with elastomers: a) NBR, b) NBR + 0.3 DPG phr.](image)

Explaining the adhesive interaction between polymers, several theories were considered: mechanical, electronic, diffusion, adsorption, and chemical. In this case, the most preferable is the formation of chemical bonds at the interaction interface was confirmed by IR spectroscopy. Thus, the strength of the adhesive interaction between elastomers and UHMWPE largely depends on the composition of the vulcanization group. With the correct combination of vulcanization accelerators, sulphide bonds are formed between the rubber macromolecules and UHMWPE. It leads to an interaction between the elastomer and UHMWPE at the chemical level. Such joints have high strength, and such materials recommended for widespread use in industry.

4. Conclusions
The development of frost-resistant elastomeric materials for sealing purposes for Arctic applications is a complex process that requires many factors determined by the operating conditions (climate, product type, working environment, load, etc.). Based on years of research, we developed approaches that have made it possible to create materials with high frost resistance in combination with oil and wear resistance (patented materials: US 8,841,370 B1; US 8,822,579 B1; RU 2 705 069 C1; RU 2 615 416 C2; RU 2 641 816 C2; RU 2 664 405 C1). The materials were successfully tested in the climatic conditions
of the Yakutia. In this study, there are examples of similar recently developed elastomeric composites. The materials were created based on both traditional BNKS NBR materials and the new frost resistant Hydrin T6000 GPCO rubber. By comprehensively affecting the structure and vulcanization parameters of rubbers by introducing oxygen-functionalized carbon nanotubes or specially prepared additives of natural origin, it was possible to improve the operational properties, wear resistance, and some other properties of the obtained elastomeric composites maintaining high frost resistance. The materials with extended functionality were developed by combining several different polymers in one elastomer. We obtained material based on NBR elastomer and wear-resistant UHMWPE plastic with combined properties. The thickness of the UHMWPE layer can be varied within wide limits – from applying thin coatings on a finished rubber product to obtaining duplicated materials, where the thickness of the elastomeric material and thermoplastics comparable. This expands the range of this method. In this case, high adhesion between layers achieved by the introduction of DPG, which ensures the crosslinking of materials at the interface. All investigated materials were recommended for implementation on the territory of the Russian Federation.

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