Evaluation of the performance of sealing rubbers operated in conditions of abrasive wear and low temperatures

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Abstract. The studied materials based on the new rubbers of unique frost resistance - propylene oxide rubber (Tg = -74 °C) and Hydrin T6000 epichlorohydrin rubber are recommended to be used as static and dynamic sealing parts for the equipment operated in the North. This was based on the full-scale tests in cold climates (Republic of Sakha (Yakutia)) and evaluation of tribological characteristics (coefficient of friction) at negative temperatures. The standard techniques were used in assessing of the changes of the physical and mechanical, relaxation, and low-temperature characteristics of model rubbers after aging. A special testing unit and a method for conducting the tests were developed to estimate the coefficient of friction at low temperatures.

1. Introduction

Elastomeric materials (rubbers) are widely used to produce various components for sealing purposes like gaskets, cuffs, rings for various machines and mechanisms. And this is due to a unique combination of properties, determined by the structural features of the elastomers. High elasticity, the ability to withstand significant repeated deformations, low modulus and ductility - all this makes rubber an indispensable material for sealing purposes. Depending on the chemical structure of the elastomers, they can have several specific properties, for example, resistance to aggressive environments, wear resistance or frost resistance. The latter properties are especially relevant for sealing rubbers operating in cold climates at extremely low temperatures (up to -60 °C), with significant cyclic daily and annual changes in ambient temperature.

The theory and practice of assessing the properties of rubbers in laboratory conditions are quite well developed. However, the data obtained do not always reflect their performance in real operating conditions, due to a complex combination of climatic and working factors determined by the characteristics of the functioning of the mechanism or unit (pressure, temperature, abrasion etc.). The use of climate chambers that allow setting a cyclic change in temperature, to some extent bring researchers closer to solving this problem. However, even the most modern climate chambers are not able to reproduce the whole variety of factors affecting the product in real operating conditions. To assess the performance of rubbers in the extreme climatic conditions of the North, it is necessary to conduct full-scale tests, which are the most reliable source of information about changes in the properties of materials and products. Earlier, we developed a methodology for assessing the performance of sealing rubbers under conditions of exposure to hydrocarbon media and naturally low temperatures. It included the determination of the main properties characterizing the performance of
rubbers in the process of full-scale exposure. Among them there are tensile strength, degree of swelling in the working medium, accumulation of compression set, coefficient of frost resistance [1]. The problem statement was determined by a wide range of stationary sealing rubber products operating in contact with fuel and oils. However, for products operating in conditions of abrasive wear (movable sealing parts, parts of pumps operating with liquids contaminated with mechanical impurities), those indicators are not enough. It is necessary to evaluate the change in the coefficient of friction of materials and their wear resistance under the influence of low temperatures. With decreasing temperature, the relaxation processes slow down, the mechanical properties and hardness of the materials change, which leads to a change in the parameters characterizing the processes of friction and wear of rubber. Therefore, the complex of climatic field tests was supplemented by the study of rubber wear depending on the pressure, sliding speed and temperature, which varied in the range +22°С to -27°С. Based on a standard friction machine equipped with a cooling chamber at the Ishlinsky Institute for Problems in Mechanics of the RAS there were developed special techniques [2-3] that allow to evaluate the coefficient of friction of elastomeric materials at negative temperatures. All this made it possible to comprehensively characterize the state of the elastomeric material and, with a higher degree of reliability, evaluate the possibility of using rubbers as moving sealing parts operating in cold climates.

2. Materials and methods

This study provides a comparative analysis of the properties of rubbers based on rubbers of different chemical nature based on full-scale exposure and studying their friction coefficients at low temperatures. The investigation was performed due to the need to search for promising frost-resistant elastomers that work in cold climates. New promising materials were studied based on propylene oxide and epichlorohydrin rubbers containing ether bonds in the main chain, which provides high flexibility and mobility of macrochains. Propylene oxide rubber (SKPO) is a new Russian elastomer, a copolymer of propylene oxide and allyl glycidyl ether. It has a glass transition temperature $T_g = -74^\circ$C. Hydrin T6000 epichlorohydrin rubber (Zeon, Japan) belongs to the same rubber group as SKPO and is a terpolymer containing propylene oxide, epichlorohydrin and allyl glycidyl ether. $T_g$ of the Hydrin T6000 epichlorohydrin rubber is -60 °C. For comparison, the data for the one of the most common rubbers for use at low temperatures was presented. It is a V-14 grade rubber based on BNKS-18, nitrile butadiene rubber with a low acrylonitrile content. The glass transition temperature of this rubber is close to -50 °C.

To assess the performance, rubber samples based on SKPO, Hydrin T6000 and BNKS-18 were placed in oil for the full-scale test in the climatic conditions of the city of Yakutsk (monthly average air temperatures for this period were close to long-term average values). Periodically, rubber samples were removed from oil and subjected to various tests: tensile strength (GOST 270-84), compression set (GOST 9.029-84), coefficient of frost resistance according to elastic rebound after compression (GOST 13808-79), degree of swelling in hydrocarbon medium (GOST 9.030-74). The rubbers contained all the necessary ingredients: fillers, vulcanizing agents, vulcanization activators and accelerators, plasticizers, antioxidants. An experimental study of the friction coefficients and wear resistance of rubbers was carried out on a UMT-2 tribometer according to the ring-disk contact scheme. Frictional interaction of the rubber specimen with a metal counterpart was carried out under the influence of normal pressure in the range 0.1–0.4 MPa and sliding speed in the range 1–100 mm/s at temperatures from room temperature to -27 °C. In addition, for the studied rubbers, the volumetric wear values at room temperature on a MI-2 friction machine were determined with a 2600 g load, for 300 s, using 80-100 microns grain size (P150) sandpaper (GOST 23509-79).

During full-scale tests all samples of the studied rubbers were placed in separate containers isolated from the environment. The containers were filled with oil from the Talakan field with density 859.5 kg/m³ at 20 °C and -39 °C pour point. The containers with samples were placed in an unheated warehouse of the climatic range of M.K. Ammosova NEFU (Yakutsk). The duration of tests in a hydrocarbon medium varied from a year to 2 years.
3. Results and discussion
During the interaction of rubbers with the hydrocarbon medium due to diffusion, the medium penetrated into the elastomer, which led to swelling of the samples. At the same time, substances soluble in the medium were extracted, which led to the mass and volume decrease of the samples. The degree of swelling is an average value reflecting the exceeding of one of these processes. At the positive degree of swelling, the swelling processes exceeded and at the negative degree of swelling the washout of ingredients (Figure 1). Like all diffusion processes, these processes depend on the ambient temperature (seasonal and daily fluctuations). The main ingredient redistributed in these processes was a plasticizer. Plasticizer is an additive that improves flexibility, mobility of macromolecules and increases the frost resistance of the material. For rubbers containing significant amounts of plasticizers (more than 10 phr), their washout has a significant negative effect on the operation of materials and parts at low temperatures.

![Figure 1. Change of the degree of swelling of rubber based on SKPO (1), V-14 grade rubber based on BNKS-18 (2) and the change of ambient temperature (3) during full-scale test.](image1)

The maximum degree of swelling in oil throughout the full-scale test does not exceeded 12-14% (Figure 1,2) for Hydrin T6000 and SKPO based rubbers due to the lower resistance to hydrocarbons, compared with BNKS-18. V-14 is one of the most common rubbers for arctic use, characterized by a significant amount of plasticizer (30-40 phr) and carbon black (120 phr). High degree of filling provides a low degree of swelling at the initial stage. But as a result of washing out the dibutyl phthalate plasticizer, the samples shrink, which can adversely affect the operation of parts and products made of this material.

![Figure 2. Change of the degree of swelling of rubber based on Hydrin T6000 (1) and the change of ambient temperature (2) during full-scale test.](image2)
Change of the swelling degree of rubbers depending on the ambient temperature leads to a change in other properties characterizing operability: tensile strength, compression set, and frost resistance coefficient. However, the strength characteristics and compression set for the full-scale test period did not undergo significant changes. Despite certain daily and seasonal fluctuations, the values of these indicators did not go beyond the standard values.

Figures 3 and 4 show the dependences of the coefficient of frost resistance according to elastic rebound after compression for rubbers based on SKPO and Hydrin T6000 on the duration of full-scale test duration in oil at ambient temperatures of the Republic of Sakha (Yakutia).

**Figure 3.** Dependence of the coefficient of frost resistance according to elastic rebound after compression on time of full-scale test: 1 – SKPO based rubber at -30 °C; 2 – SKPO based rubber at -50 °C.

**Figure 4.** Dependence of the coefficient of frost resistance according to elastic rebound after compression on time of full-scale test: Hydrin T6000 based rubber at -30 °C (1); Hydrin T6000 based rubber at -50 °C (2).
Propylene oxide and epichlorohydrin rubbers contain ether bonds in the main chain. This provides high elasticity and recoverability at low temperatures. Throughout the entire full-scale test period, consistently high values of the coefficient of frost resistance were observed. $K_M$ values for rubber based on SKPO at all studied temperatures were slightly higher than for rubber based on Hydrin T6000. Both rubbers showed unique frost resistance despite the difficult temperature conditions of the test (extremely low temperatures down to $-45 \div -50 ^\circ C$, daily diurnal temperatures up to $30 ^\circ C$ in the autumn-spring period).

The main negative effect of diffusion processes influenced on the frost resistance of rubber based on BNKS-18. This rubber has the highest glass transition temperature ($T_G = -50 ^\circ C$) among all investigated rubbers. Addition of significant amounts of plasticizer can increase the coefficient of frost resistance to acceptable values. However, in contact with oil, the plasticizer intensively washed out (Figure 5). This led to a sharp irreversible drop of the frost resistance at critical operating temperatures. The $K_V$ values of V-14, measured at $-50 ^\circ C$ after a year of exposure do not exceeded 0.1. Thus, the probability of failure during operation in harsh climatic conditions of the Republic of Sakha (Yakutia) for BNKS based products is high.

![Figure 5. Change of the coefficient of frost resistance (1) and dibutyl phthalate plasticizer content (2) of V-14 rubber based on BNKS-18 and the change of ambient temperature (3) during full-scale test.](image)

Thus, according to the data obtained during full-scale tests of rubbers close to the actual operating conditions, a complex change in the main operational properties occur. If tensile strength and compression set of rubbers do not undergo significant changes, then frost resistance cannot be predicted based on laboratory tests only. Such conditions as harsh extremely continental cold climate, cyclic changes in temperature with a transition through $0 ^\circ C$ twice a day in the spring-autumn period lead to intensification of diffusion processes. This enhances the plasticizers washout and reduces the coefficient of frost resistance. For the rubber based on BNKS-18 $K_V$ at $-50 ^\circ C$ irreversibly dropped to 0 in the first months of exposure. The rubbers which low-temperature elasticity at critical operating temperatures ($-45 ^\circ C$ and below) determined by elastomer (Hydrin T6000 and SKPO) showed excellent low-temperature characteristics. A stable and reliable operation can be expected for the parts and products from these rubbers.

In some cases, it is important to consider not only the influence of an aggressive hydrocarbon environment and climatic conditions, but also the effect of abrasives, material wear due to contact with working metal surfaces. This is especially important for rubber seals operating as part of movable seals, pulp and contaminated media pumps etc. It is about changing the tribological characteristics of the elastomeric material at low temperatures. These processes are practically not investigated and can
have a significant impact on the performance of rubber products and parts. Scientists at the Ishlinsky Institute for Problems in Mechanics of the RAS and M. K. Ammosov NEFU were the first to conduct studies of the dependences of the coefficient of friction of rubbers on temperature, sliding speed and normal load [2–4]. On the special testing unit developed based on the UMT-2 tribometer, various loads and temperatures can be created in a wide temperature range (down to -25 °C). The dependences of the dynamic coefficient of friction for rubbers based on SKPO, Hydrin T6000 and BNKS-18 on sliding speed and bulk temperature are shown in Figure 6. Tests of rubber samples were carried out at four pressure levels. However, in order to simplify the presentation of the analysis results Figure 6 presents data for two extreme pressures of 0.1 and 0.4 MPa and two temperatures of +22 and -25 °C.

![Figure 6](image-url)

**Figure 6.** The friction coefficient \( \mu \) versus sliding velocity \( V \) at two bulk temperatures for different types of rubber: a BNKS-18 (V-14), b Hydrin T6000 and c SKPO, where curve 1 corresponds to nominal pressure 0.1 MPa and curve 2 to 0.4 MPa.

The process of abrasive wear is usually considered as a set of multiple single acts of micro-cutting or micro-tear, i.e. it usually depends on the chemical structure, strength properties and stiffness of the polymer. Propylene oxide and epichlorohydrin rubbers have a similar chemical structure. The rubbers based on them were characterized by a similar composition and low degree of carbon black filling (not more than 60 phr), which led to close values of the coefficient of friction of rubbers at room temperature at low sliding speeds. The values ranged from 0.2 to 0.6. Then, with an increase of the sliding speed, the friction coefficient of Hydrin T6000 rubber increased significantly compared to rubber based on SKPO. This was associated with the features of the material composition. For rubber based on SKPO, the values of the friction coefficient at all loads, sliding speeds, and temperature were significantly lower than for rubber based on Hydrin T6000 and BNKS-18 (Figure 6, a,b). Rubber based on BNKS-18 was characterized by high values of \( \mu \) at room temperature, which is 4.2–4.8 times higher than for rubber based on SKPO and 2–4 times higher than for rubber based on Hydrin T6000 (Figure 6, c). However, at a temperature of -25 the differences were not so significant.

Table 1 shows the tensile strength, elongation and volumetric wear of the investigated rubbers. The lowest values of the coefficient of friction of rubber based on SKPO correlated with the lowest value of volumetric wear, which is confirmed by published data [5]. The data indicated that at “constant normal load and sliding speed, the abrasion during abrasive wear on the MI-2 friction machine decreases with decreasing coefficient friction, as well with an increase of the tensile strength and elasticity of rubber”. Despite the high coefficient of friction, V-14 rubber based on BNKS-18 had higher tensile strength compared to Hydrin T6000 based rubber and slightly lower volumetric wear values due to the high degree of carbon black filling. It is known [5] that active fillers provide increased wear resistance due to the formation of carbon black-rubber gel during addition of carbon black and formation of many rubber-carbon black bonds.
Table 1. Main properties of the investigated rubbers

| Rubber base | $f_p$, MPa | $\varepsilon_p$, % | $\Delta V$, cm$^3$ |
|-------------|------------|-------------------|-----------------|
| SKPO        | 8,8        | 187               | 0,91            |
| Hydrin T6000| 7,1        | 344               | 1,33            |
| BNKS-18     | 9,0        | 223               | 1,29            |

The results of studying the coefficient of friction of the rubbers at negative temperature (Figure 6) can be considered interesting and new. At -25 °C, the friction coefficients of SKPO based rubber were slightly increased and lied in 0.4–0.6 range at all investigated loads and sliding speeds. The scatter of values was minimal, which suggests high wear resistance and stable operation of materials and at low temperatures. An increase of the coefficient of friction was also observed for Hydrin T6000 rubbers with temperature decrease. The values of the coefficient of friction ranged from 0.6 to 1.0. For V-14 rubber, an increase in the coefficient of friction at -25 °C was small in absolute value, which can also be explained by the composition of this material and the increased content of carbon black. Change in the friction coefficients is likely to entail a change in the wear resistance of the material.

4. Conclusions

Thus, lowering the temperature to negative values significantly affects the properties, primarily, wear resistance and frost resistance of elastomeric materials. Such changes must be considered when predicting the performance of rubbers in real operating conditions. The obtained results allow us to characterize the change in the physical and mechanical, low temperature, and tribotechnical properties of model rubbers based on new frost-resistant elastomers, as well as to assess the possibility of their use in extremely low temperatures of the northern regions of the Russian Federation. The developed approaches can be recommended for widespread use, as they provide the most objective information on the performance of rubbers. This can become very valuable in the absence of information on large-scale studies of the performance of standard seals in machines and mechanisms. Materials based on propylene oxide and epichlorohydrin rubbers showed high level of frost resistance during full-scale tests and low values of friction coefficients at low temperatures. They should be recommended for implementation and application for the manufacture of both fixed and moving sealing parts of North equipment.

Acknowledgments

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