Reduction of negative environmental impact of mechanisms by improving tribotechnical indicators of sealing materials

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Abstract. In order to eliminate the negative environmental impact of transport and mechanisms operating under high speeds and loads, high abrasion wear, composite materials for sealing devices, thrust bearings, Goodrich stern bearings have been developed by the interaction of nitrile butadiene rubber with novolac resin, cured with dinitrile. The physico-mechanical and tribotechnical data of laboratory and production tests of the developed composites are shown.

1. Introduction
The life cycle of equipment and machinery is often determined by the wear of friction units. The task of increasing the service life of friction units of machines and mechanisms at high speeds and loads under conditions of abrasive wear must be solved by creating composite materials with high self-lubricating and wear-resistant properties.

This will result in a significant reduction in downtime of vehicles and equipment, will help to limit the leakage of oils and hydraulic fluids by increasing the tightness of sealing materials and will reduce negative environmental impact.

In many cases, polymeric materials with the desired set of properties can be obtained significantly easier by selecting the right mixture of polymers than by synthesizing new ones.

Early studies were aimed at modifying polystyrene, but for a long time many other polymers, including such thermo-plastics as phenol-formaldehyde resins, have become the subject of researches [1]. At the same time, the formation of semi-interpenetrating polymer networks is possible by structuring a thermo-plastic on the matrix of a linear polymer. The components of such a mixture are inseparable because of the mechanical interlacing of chains [2, 3]. In addition, the chemical interaction of functional groups can lead to a noticeable increase in the strength characteristics [4, 5].

We have previously described the catalytic hardening of novolac resin with aromatic dinitriles [6, 7]. It is of interest to study the interaction of nitrile-butadiene rubber with novolac resin in order to obtain rubber products with increased strength and tribotechnical characteristics.

2. Experimental part
In this work, industrial samples of butadiene-nitrile rubber of the SKN-3825, SKN-3826, V14 brands manufactured by KRASELAST, Krasnoyarsk, TU 2512-046-00152081-2003 gr. III-1b-23 were used.
2.1. Novolac resin GOST 18694-80

Coke-graphite mixture (CGM) was obtained by joint grinding of coke and electrode graphite in a ball mill and following sifting to particles of 250–500 microns.

A brief process procedure for obtaining a polymer-polymer mixture of nitrile-butadiene rubber and novolac resin is the following list of operations:

- Novolac resin was heated in a steel container up to 80-90 °C until complete melting and then 8-12 wt.% of dinitrile were introduced. The mixture was stirred until the hardener was completely dissolved and cooled to room temperature, then it was ground to a powder;
- the prepared Novolac resin was mixed with crude rubber (nitrile butadiene rubber SKN-3825, SKN-3826, V14) on a screw extruder, followed by rolling in a proportion of 70-80 wt. % rubber and 20-30 wt. % novolac.

Samples for deformation-strength tests were obtained by pressing at 150-160 °C and pressure of 35 ± 5 MPa for 10-15 minutes. The tensile strength (GOST 11262-80) was determined on a universal machine Instron 3367 (USA). The determination of microhardness (GOST 20403) was carried out on a microhardness tester 2034 TMR.

The friction coefficient was determined on the friction machine MI-2, the counter-body was steel 45, the specific pressure was 0.2 MPa, and the sliding speed was 0.32 m/s for friction without lubricants. The IR spectra were recorded on an ALPHA IR spectrometer (Bruker, Germany) in the range of wave numbers 4000–600 cm\(^{-1}\) (the ATR attachment, ZnSe crystal).

Diffusion-chrome-plated steel-45 was used as the material of the counter-body to the polymer material.

3. Results and discussion

To study the features of the interaction of industrial samples of nitrile-butadiene rubber with novolac resin, mixtures of these substances containing different amount of resin were prepared. The interaction of phenol-formaldehyde resin and nitrile-butadiene rubber can be represented as follows:

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\begin{align*}
\text{OH} & \quad \text{OH} & \quad \text{CH}_2\text{OH} + \text{N}\equiv\text{C} \quad \text{CH}_2\\
\text{OH} & \quad \text{OH} & \quad \text{CH}_2\text{OH} + \text{N}\equiv\text{C} \quad \text{CH}_2
\end{align*}
\]

The reaction takes place between the methylol group of the resin and the nitrile group of rubber. Unshared electron pairs of the oxygen atom of the hydroxyl group of the phenol are involved in the p-π conjugation with the benzene ring. As a result, the nucleophilicity of this atom is noticeably lower than that of the oxygen atom in the methylol group. The structuring of the thermoset plastic on the linear elastomer matrix occurs in the process of hot direct pressing due to the interaction of the nitrile group of rubber and the methylol hydroxyl group of the novolac resin with the formation of a new intermolecular azomethine bond. Figure 1 shows the dependence of tensile strength of the obtained materials on the concentration of novolac in the mixture. With the introduction of 5 wt. % of novolac, there is a significant increase in strength for rubber SKN-3826 and 3825. The maximum value is observed in the filling area of 15 wt. %. At the same time, for SKN-3825, the tensile strength increases
by 40-42 %, for SKN-3826 - by 53-56 %, for V14 - by 19-20 %. A further increasing the resin content leads to a decrease in strength, possibly because the mixture of novolac is exposed to incomplete interaction, the excess part forms separate conglomerates, leading to heterogeneity, and their size will increase with the growth of the unreacted part.

Figure 1. The dependence of the tensile strength of vulcanizate $\sigma_p$ (MPa) on the concentration of novolac in the mixture: 1 - SKN-3825, 2 - SKN-3826, 3 - V14.

The IR spectra of the rubber-resin vulcanizate containing 15 wt. % Novolac indicate the presence of the highest intensity of C = N-bond at 1690 cm$^{-1}$, and the absorption of the hydroxyl and nitrile groups presented in the spectra of the original polymers is significantly reduced. Judging by the insignificant absorption at 2240 cm$^{-1}$, corresponding to the C≡N bond, there is no complete structuring, which can be explained by significant diffusion difficulties due to a reduction in the segmental mobility of the interacting polymers. The depth of the process is $\sim$ 72.5 %. Increasing the amount of rolling of the mixture did not lead to a noticeable improvement, and an increase in the duration and temperature of the process, possibly due to degradation, leads to the opposite effect.

Figure 2. The dependence of the relative elongation at break of vulcanizate $\varepsilon_p$ (%) on the concentration of novolak in the mixture: 1 - SKN-3826, 2 - SKN-3825, 3 - V14.
As expected, as the rubber is filled with the Novolac resin, there is an almost linear decrease in the relative elongation at break (Figure 2). The decrease in elasticity due to crosslinking of polymer units at 15 wt. % resin content is 33-35 % for all studied rubber grades.

Determination of the hardness of the obtained resin-rubber composites showed an almost linear dependence of the increase in hardness with increasing novolac content (Figure 3). With the optimal introduction of novolac (15 wt. %), the hardness of the obtained composites according to Shore increases from 60-65 to 80-25 for rubber brand SKN-3826 and from 76-84 to 90-93 units for rubber brand SKN-3825.

Figure 3. The dependence of the microhardness of vulcanizate on the percentage of filling novolak: 1 - SKN-3826, 2 - SKN-3825, 3 - V14.

In order to obtain composites for antifriction purposes, a method for introduction of a coke-graphite mixture into the resin-rubber vulcanizate was proposed. SKN-3825 rubber was chosen as a base. The introduction of CGM into a resin-rubber vulcanizate when mixed on an extruder followed by rolling did not lead to a homogeneity of a system. Therefore, it was decided to introduce a solid lubricant into the solution of novolac, followed by mixing with rubber. For this reason, the powder of novolac was dissolved in acetone or a solution of ethyl alcohol. To reduce the amount of solvent, the optimal composition is selected: 1 cup. solvent for 2 w.p. novolak powder. The CGM was injected in the prepared solution to obtain a thick pasty mass. In the end, a composite containing 1 of novolak at 2.0-2.2 w.p. CGM was obtained. The obtained filler was dried and mixed with crude rubber.

Deformation-strength tests of the obtained material showed that with the introduction of resin-CGM in rubber up to 40 wt. % filling, an increase in strength at break by 12-14 % with a decrease in elasticity by 50 % is observed. Then there is a sharp loss of strength and elasticity, due to the saturation of the polymer matrix with filler.

The introduction of CGM into the vulcanizate significantly affected the reduction of the friction coefficient and the intensity of wear. As seen in Figure 4, the introduction of a solid lubricant even with small quantities leads to a significant decrease in the coefficient of dry friction on steel. The minimum value of 0.17 is observed at 40-50 wt. % content of the filler.
Figure 4. Dependence of the friction coefficient $\mu$ on the content of resin-CGM in the composite.

The obtained material was used for rubberizing the thrust bearings and barrel of a submersible water lifting pump at the Municipal Unitary Enterprise «Vodokanal» in Ulan-Ude, work of which is accompanied by an increase in abrasive wear of friction units (Figure 5). In the process of rubberizing the barrels, the improved fluidity of the composite raw vulcanizate is established in comparison with pure raw rubber, which simplifies filling the molds of great height, for example, for the manufacture of Goodrich stern bearings.

Figure 5. Rubberized sliding bearings of a water lift pump.

Conducted performance tests showed high reliability of the obtained composition (rubber-resin-graphite-coke vulcanizate). Thus, the life cycle (within 12 months) of the thrust bearings made by us is 2.5-3.0 times higher than the factory analogues, while the presence of impurities of wear products in water is almost not detected.

4. Conclusion

The complex of operational characteristics of the developed materials based on industrial nitrile-butadiene rubber, novolac resin and solid lubricant filler in the form of a coke-graphite mixture makes it possible to use in tribotechnical devices in the form of movable seals and sliding bearings, Goodrich stern bearings, exploited without lubrication at high speeds and loads and high level of abrasive wear.
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