Mechanical Properties and Deformation Features of Nitrile Butadiene Rubber with Protective Coating from Ultra High-Molecular Weight Polyethylene

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Abstract. The influence of the duration of the rubber preliminary vulcanization on the physicomechanical properties, wear resistance and hardness of nitrile butadiene rubber with a thin protective coating from ultra-high molecular weight polyethylene are studied. The optimal duration of the preliminary vulcanization of the rubber providing high adhesive interaction between the rubber and the coating was established. High adhesive interaction leads to an increase in abrasion resistance while maintaining the physical and mechanical properties of the original rubber. Structural rearrangements under uniaxial tension of ultra-high molecular weight polyethylene coated on a rubber surface were visualized using atomic force microscopy. The formation of ordered fibrils on the surface of ultra-high molecular weight polyethylene after 30% elongation is shown.

1. Introduction
Rubber is widely used in sealing devices due to its highly elastic characteristics - the ability to large reversible deformations when relatively small loads are applied, practical incompressibility (Poisson's ratio is close to 0.5), low density, high internal friction and energy intensity [1]. Depending on the functional purpose, rubber seals are usually divided into seals for movable and fixed joints and seals that perform the function of command and control devices (valves, membranes, diaphragms, etc.) [2].

Stringent requirements on the properties, which must ensure working at high speeds, under friction in a chemically aggressive environment, in a stress-strain state etc. are imposed for movable joints sealants. However, most rubbers cannot fully meet all these various requirements in their original form. Therefore, research aimed at finding new ways to modify rubber in order to improve certain characteristics, while maintaining the original unique properties of rubber, are extremely relevant.

One of the effective ways to increase the wear resistance of rubbers is surface modification with a protective coating. A large number of different coating methods are known [3-7]. This work is devoted to the study of the effect of coating technology on the technical properties of coated rubbers, which largely depend on the adhesive interactions between the protective coating from ultra-high molecular weight polyethylene (UHMWPE) and nitrile butadiene rubber (NBR). It is known [1], that all seals of movable joints operate at 30–40% strain to ensure tightness. Therefore, maintaining the integrity of the surface of the protective coating during deformation of rubber should be researched. Atomic force
AFM microscopy [12–13] was used to study the processes occurring on the surface of coated rubber during deformation. The process of changing the surface structure of UHMWPE coated on the surface of NBR is visualized under uniaxial tension [8–11].

2. Experimental details
NBR with a minimum content (17-19%) of bound acrylonitrile (ACN) was used to apply a protective coating. It is known [14] that the basic properties of NBR depend on the content of ACN. A decrease in the ACN content leads to an increase in elasticity and frost resistance, and to a decrease in heat generation during repeated deformations. However, at the same time, the elastic-strength properties, wear resistance, hardness, aggressive resistance, as well as resistance to heat are reduced. Therefore, a thin protective coating from UHMWPE GUR-4113 with a molecular weight of 3.9x10^6 g/mol is applied to increase the wear resistance and hardness of frost-resistant NBR. UHMWPE GUR-4113 has a high resistance to wear and aggressive environment, including at extremely low temperatures [15-17]. The UHMWPE protective coating is hot pressed. The average thickness of the UHMWPE coating is 50-60 μm (Fig. 1).

A coating method [18] based on the use of preliminary vulcanization of the rubber has been developed to increase the adhesive interaction between the coating and the matrix. The method is described in more detail in [19]. An important functional purpose of pre-vulcanization is the removal of surplus rubber (flash) during hot pressing. If there is a surplus rubber, then UHMWPE is squeezed out of the mold together with a flake, which leads to the formation of uncovered sections on the rubber surface.

Rubber compounds were mixed by a Polymix 110L laboratory roll using a W50 EHT mixer with oval (tangential) Banbury rotors according to the regime adopted for standard rubber. Curing was done in 155°C for 20 min.

The AFM study of the deformation of coated rubbers was carried out using a stretching device [20] developed for the Ntegra Prima AFM (NT-MDT, Russia). A schematic illustration of a stretching device with a fixed sample is shown in Fig. 2.
The AFM study of deformation using the device is carried out as follows: A sample is fixed to traverses and the device is installed in the AFM positioner. After the preliminary standard procedures (starting the control program, turning on the device, installing the probe sensor, setting up the cantilever deviation registration system, installing the sample, installing the measuring head, manually supplying the sample to the probe at a distance of 0.5-1 mm), the sample is automatically brought to the working distance (1-2 nm) and scanning of its surface is carried out. Then, the sample is returned to a safe distance for the probe (0.5-1 mm) and the sample is stretched to a certain length. Then the procedure is repeated (supply and scanning of the sample). Such a cycle can be repeated several times. In order to keep the probe above the same region of the sample all the time, the deformation and scanning processes are controlled using AFM optics. Usually, a scan is performed near a specific defect on the surface selected as a marker. Thus, it is possible to obtain a series of scans of a certain part of the sample surface at different elongation.

Physical and mechanical studies of coated rubber samples were carried out on a UTS test machine (Germany) in accordance with GOST 270-75 (ASTM D638). The abrasion resistance of coated rubbers was evaluated in accordance with GOST 23509-79 (ASTM D 5963) on MI-2 friction machine. Electronic images of the NBR and UHMWPE microstructure were obtained using a JEOL JSM-7800F scanning electron microscope.

3. Results and discussion
The study of the physicomechanical properties of the coated rubbers showed that the duration of the preliminary vulcanization of the rubber has an effect on the elongation and tensile strength of the coated rubbers (Fig. 3). Preliminary vulcanization up to 4 min leads to a decrease in elongation and tensile strength. However, starting from 5 min, there is an increase in elongation at break and tensile strength.

![Figure 3. Effect of the duration of pre-vulcanization on the physical and mechanical properties of coated rubber.](image)

The change in physical and mechanical properties depending on the duration of the preliminary vulcanization can be explained by the formation of a spatial network of the rubber during vulcanization (crosslinking of the rubber). The vulcanization temperature of NBR (150-160°C) [3] and the melting temperature of UHMWPE (from 135°C) [21] are in the same range. Therefore, UHMWPE passes into a highly elastic state in the process of vulcanization and penetrates into the rubber forming a strong joint until the rubber is completely crosslinked. In the case of preliminary vulcanization up to 4 min, the spatial network of the elastomer is not completely formed, which allows UHMWPE to penetrate into the rubber locally with the formation of clusters (Fig. 4). These clusters serve as stress concentrators under mechanical stress and lead to destruction. This causes a decrease in elongation at break. An increase in the degree of crosslinking after 5 minutes of preliminary vulcanization leads to an increase in the density and hardness of rubber, which increases pressure on UHMWPE and leads to the formation of stronger bonds of macromolecules inside UHMWPE. An increase in the elastic-strength properties of a thin coating of UHMWPE is reflected in an increase in the physical and mechanical properties of coated rubbers.
Figure 4. SEM images of the surface (a) and low-temperature chip (b) of a coated NBR with preliminary vulcanization for 3 min.

Fig. 5 shows the effect of pre-vulcanization of the rubber composition on volumetric loss during abrasion and shore hardness A of coated rubber. Shore A hardness increases as the duration of pre-vulcanization increases. As expected, the abrasion resistance of coated rubber is much greater than the resistance of the original rubber. The smallest volume loss is observed for coated rubbers with preliminary vulcanization up to 4 min (0.052 cm³), which is 5 times lower than the volume loss of the original rubber.

Volume loss decreases as the duration of pre-vulcanization increases up to 5 min. But starting from 5 min it gradually rises. The most intense increase in volume loss is observed starting from 7 min. It is possible that the increase in volume loss during friction is associated with a decrease in the adhesive interaction between the coating and rubber. A decrease in adhesion can also be associated with the formation of a spatial network of rubber. An increase in the duration of preliminary vulcanization over 7 min leads to an almost complete formation of a spatial network, which prevents the interaction between rubber and UHMWPE. Low adhesive interaction between NBR and UHMWPE leads to delamination of the coating from rubber under abrasive action.

Therefore, as a result of a study of the physical and mechanical properties, wear resistance, and hardness of the coated rubbers, it was found that a time range of 4 to 6 min is the most optimal duration of preliminary vulcanization for a UHMWPE coating on NBR.

An AFM study of the surface of coated rubbers was carried out to detect the initial stages of the formation of micro-fractures during deformation and to describe the mechanisms of reconstruction of the surface microstructure of the UHMWPE coating. The study was conducted in the tapping mode, using the NT-MDT cantilever HA_NC Etalon. A sample with 6 min of preliminary vulcanization, which showed the best combination of technical properties due to the high adhesive interaction with rubber, was chosen for AFM studies of deformation.
Fig. 6 shows the surface topography of UHMWPE coated on the surface of NBR. The scan size is 100x100 microns. Spherical formations with a diameter of about 60 microns are observed. Perhaps this is the shape of the UHMWPE powder particles, which are interconnected under high temperature during joint vulcanization with rubber. In the regions where the UHMWPE particles are connected, microdepressions are observed. The depth of the microdepressions is approximately 2–3 μm.

![Figure 6. 3D topography of UHMWPE coated on the surface of the NBR.](image)

Fig. 7 shows the visualization of the surface reconstruction of UHMWPE coated on the NBR under uniaxial tension. Scans of the same area on the surface of UHMWPE after stretching by 0, 20, 30 and 100% are shown. After 30% stretching anisometric formations (fibrils) on the surface of UHMWPE appear along the axis of stretching. The direction of stretching is horizontal.

![Figure 7. The formation of fibrils on the surface of UHMWPE under uniaxial tension.](image)

It was shown that the detected fibrils stretch with increasing elongation. The interfibrillar distance increases and the transverse size of the fibrils decreases (Fig. 8). It was found that an increase in stretching by 70% leads to a decrease in the transverse size of the observed fibrils, on average, by 35% (150 nm).

![Figure 8. The formation of oriented fibrils under stretching.](image)
4. Conclusions

It was shown that pre-vulcanization of NBR for 4-6 min is optimal for its coating with UHMWPE, providing high adhesion between them, which leads to increase in wear resistance (by more than 5 times) and Shore A hardness (by 4) while maintaining physical and mechanical properties of rubber.

The AFM study showed that the integrity of the surface structure of the protective coating of UHMWPE during deformation up to 100% is not violated and the formation of microcracks is not observed. It is shown that after 30% elongation, the surface structure is rearranged and elongated fibrillar formations appear along the stretching axis.

5. References

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