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Studies of wear resistance and antifriction properties of metal-polymer pairs operating in a sea water simulator

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ABSTRACT

Introduction. Sea water is an aggressive environment that causes corrosion, erosion, and cavitation when moving at high speeds of steel, cast iron, bronze, or babbitt parts that work satisfactorily only with lubrication. In this case, oil stains are often released into the water, which leads to pollution of the water basin. **Materials and methods.** To study the wear and friction coefficient, the following materials were chosen: pure polyamide *P-610* and antifriction materials based on it *Maslyanit D* and *Maslyanit 12*. The following metals were used as the material of the counterbody: stainless steel *Cr18Ni9Ti*, bronze (9 % *Al*; 2 % *Mn*), and titanium alloy *VT-3*. **Results and discussion.** It is established that the materials of the "maslyanit" group have significantly better wear resistance and antifriction properties than pure polyamide *P-610*. It is shown that the reason for such properties of *Maslyanit D* and *Maslyanit 12* is the presence of solid and grease lubricants in its compositions, which simultaneously also play the role of a plasticizer. Finely dispersed metal fillers favorably affect the heat rejection from the friction zone and the growth of the crystalline phase of the polymer. A positive effect of iron minium on the friction of *Maslyanit 12*, which causes the generation of a protective anti-friction film on the working surfaces of the friction pair, is revealed. A decrease in wear and friction coefficient is found as the purity class of the metal surface increased. The predominantly fatigue mechanism of wear of polymeric materials during friction in a sea water simulator is confirmed. The results of testing *Maslyanite 12* in a real marine environment confirmed the positive characteristics of *Maslyanit 12*.

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Introduction

In the products of modern construction, shipbuilding, ship repair and other industries (port and deck mechanisms, technological equipment, watercraft, screw-stern and steering devices, ship centrifugal submersible pumps, equipment for oil production platforms, farms for breeding marine fish, desalination stations), which are in contact with fresh or sea water, are increasingly using polymeric materials. Sea water is a strong electrolyte; it has high electrical conductivity and aeration. The high aggressiveness of this medium, containing in its composition sodium sulfates, sodium chlorides, magnesium, calcium and other salts, cause corrosion, erosion, and cavitation when steel, cast iron, bronze or babbitt parts and assemblies

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move at high speeds. These parts and assemblies work satisfactorily only in the presence of lubrication. This often results in the re-lease of oil stains into the water, adversely affecting the fauna and flora. Ship shaft bearings (stern tube bearings) operate under extreme conditions. Solving the problem of its reliability and performance in water, especially at high pressures of the deep sea medium, is one of the difficult tasks of materials science [1, 2, 3].

Polyamides and compositions based on it have high wear resistance and a stable coefficient of friction in water and in other media; lubricants can reduce vibration loads and noise and ensure the environmental safety of the water basin. Despite the fact that the presence of a liquid medium, including water, leads to swelling of polymeric materials, it is found that exposure to water stabilizes its dimensions and improves tribological properties [4, 5].

At the same time, in the works by the school of *Rehbinder* and other researchers [6, 7, 8, 9] the adsorption effect of water and other liquids on the strength of solids due to a decrease in surface energy and its “wedging” effect on walls has become wide-spread. It is assumed that a decrease in the strength of polymers is caused by a change in the surface energy, which leads to a decrease in the critical stress at the crack tip. With this approach, failure is a critical phenomenon that occurs when the stress at the tip of the most dangerous crack reaches the strength of the material.

An approach based on the kinetic concept of strength was developed in the works of *Bershtein* [10, 11, 12], who proceeded from the kinetic concept, according to which destruction occurs as a result of the accumulation of chemical bond breaks under the action of thermal fluctuations, i.e., the destruction in the presence of water molecules is a reaction of mechanically stimulated hydrolysis.

In studies on the tribotechnical properties of polymer composite materials, we found [13, 14] that under the dry friction with an oscillating movement of the working surface, with unidirectional linear movement, in the presence of dynamic loading, in abrasive or chemically aggressive media, the leading wear mechanism is fatigue failure of the working layer. The state of the friction surfaces of the pair is characterized by the presence of a certain composition of surface films. In real air conditions, all microasperities and microcracks are almost instantaneously coated with oxide films and layers of adsorbed polymer sample molecules and fillers that are strongly bound to the metal. Typically, oxide layers are located above the juvenile (pure) surface. These films shield the working surfaces of the tribosystem thus contributing to the boundary friction mechanism in the absence of lubrication and “self-organization” of the steady-state friction [15, 16].

The materials used for the manufacture of friction parts should have low friction coefficient and high wear resistance, i.e., optimal basic informative tribotechnical characteristics. Besides, the tribotechnical composite materials require that the materials used as modifiers are able to form friction transfer films (graphite, carbon, polytetrafluorethylene, silicon dioxide, molybdenum disulfide, etc.) during friction and ensure a self-lubricating mode. These requirements can be met by the use of polymer composite materials (*PCMs*). Most polyamides are characterized by a good combination of these parameters; it retains its properties when exposed to aggressive media [3, 17, 18, 19].

The analysis of various studies shows the need for experimental verification of the behavior of polymer materials in the presence of sea water in the working contact.

The purpose of this work is to study the tribotechnical properties of materials based on polyamide in a sea water simulant medium and to compare pure and filled polyamides in terms of its antifriction properties and fatigue wear resistance under various test conditions.

This purpose requires the solution of the following tasks:

- 1) to choose the test materials on the basis of theoretical surveys;
- 2) to develop a test method and experimental equipment;
- 3) to perform laboratory tests of chosen materials;
- 4) to verify laboratory test methods in conditions simulating the actual operation modes of the product.

To ensure high reliability of friction units operating in sea water, the correct choice of a friction pair is of great importance. The increased wear observed during the operation of functional units requires new polymer-based anti-friction materials, one of the representatives of which is a group of materials called “*Maslyanit*.” Due to its unique characteristics in water medium, *Maslyanit* materials have been widely

used in hydraulic structures, port and ship mechanisms instead of rolling bearings, antifriction bronze, babbitt, caprolon. Most high-pressure hydropower plants in Russia and the CIS countries use this type of material.

Materials and methods

The following materials were selected: unfilled pure *Polyamide P-610* and antifriction materials on a polymer (*Polyamide*) basis from the group of “*Maslyanit*” – *Maslyanit D* and *Maslyanit 12*. Metals were used as the material of the counterbody: stainless steel *Cr18Ni9Ti*, bronze (9 % *Al*; 2 % *Mn*), and titanium alloy *VT-3*.

The tests were performed on the end friction machine (Figure 1). The upper head (4) with the test sample (3) is placed into a spindle (8) of the friction machine. The friction unit represents a cup (2) on self-adjustable bearings (11), into which a metal counterbody (9) fixed by a pin against rotation is placed. The friction force was determined using a strain gauge (1). Loading was ensured by a lever system (5, 6, 7) and a load (10).

A sea water simulator is poured into the cup 25–30 mm above the friction plane, prepared in the following percentage ratio (to the working medium) of the main components: (*NaCl* – 2,42 %; *CaCl₂* – 0,12 %; *NaSO₄* – 0,4 %; *Mg Cl₂* – 1,1%)·6*H₂O*. The unit was cooled from overheating with an air stream using a fan.

The test material samples represent annulus cross section plugs with slots in the form of sectors to ensure continuous access of the working medium (sea water simulator) to the friction zone. The contact ratio $K = 1/3$ (ratio of contact area to the full surface of the ring section). The shape and dimensions of

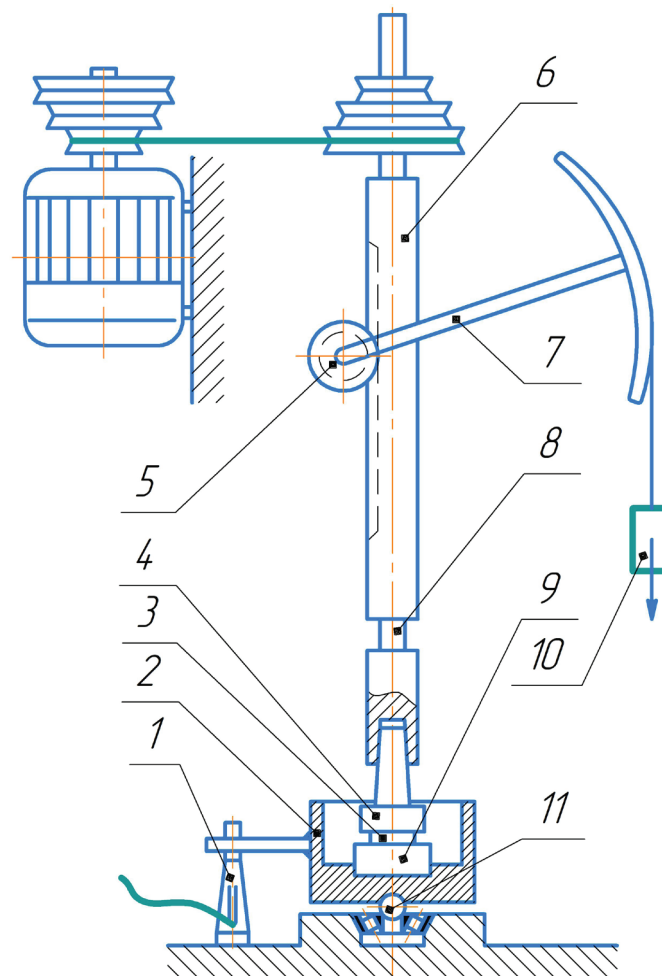


Fig. 1. End friction machine

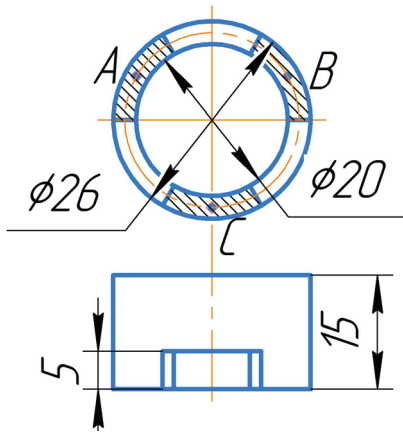


Fig. 2. Sample shape and dimensions

the sample are shown in Figure 2. The samples were manufactured by injection molding, followed by thermal and mechanical processing. The roughness of the friction surfaces of all test samples and counterbodies corresponded to class 7 ($Ra = 0.8 \mu\text{m}$).

Test method. Before the start of the experiment, the sample and the counterbody were kept for 24 hours in a sea water simulator, then degreased with gasoline and acetone. For all variants of friction pairs, comparative tests were carried out at the following modes:

- specific load $P_{sp} = 4.5 \text{ MPa}$;
- linear speed along the average radius of the sample $V = 0.14 \text{ m/s}$.

The experiment lasted 11 hours. Current measurements were made every 1 hour during the running-in of the samples in order to determine the point of transition of the running-in mode to the stationary (steady-state) wear mode and after 6 hours – after the stabilization of the process. The linear wear of the material

was measured on a vertical optimeter with an accuracy of 0.001 mm on three friction areas (A, B, C) separately and averaged.

Results and Discussion

The results of wear over time are shown in Table 1; according to the averaged values of three tests (Experiments), its graphical representation is presented in the form of histograms (Figure 3).

Table 1 and Figure 3 show that the materials of the *Maslyanit* group have better wear resistance than pure *Polyamide P-610*. It should be assumed that the reason for the high wear resistance of *Maslyanit D* and *Maslyanit 12* having the same polyamide base (matrix) is the presence of both solid and grease oil in its compositions, which simultaneously act as a plasticizer. The fillers of these compositions are fine metal powders, which increase the thermal conductivity of the material and reduce local temperatures in the friction zone [18]. In addition, the particles of these powders, being the centers of crystal formation, increase the crystalline phase of the material, which has a positive effect on its wear resistance [18, 19].

Comparing *Maslyanites* with each other, it should be noted that for *Maslyanit D*, the wear rate stabilizes after surface running-in, while for *Maslyanit 12*, even after the experimental time (11 hours), there is a large scatter of this evaluation parameter: zero wear when working with steel in one of the experiments

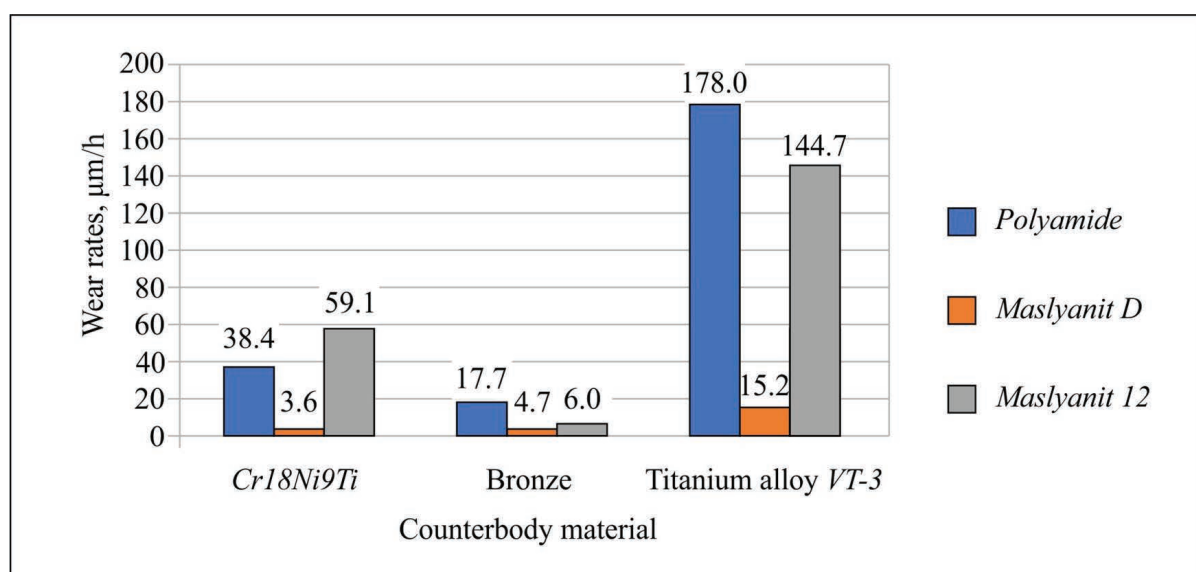


Fig. 3. Wear rates of metal-polymer friction pairs in a sea water simulator

Table 1

The results of wear resistance of metal-polymer friction pair in the sea water simulator (wear rate, $\mu\text{m/h}$)

Sample material		Steel	Bronze	Titanium alloy
<i>Polyamide P-610</i>	Experiment 1	25.0	11.6	90.3
	Experiment 2	69.0	35.6	210.0
	Experiment 3	21.4	5.9	223.0
<i>Maslyanit D</i>	Experiment 1	5.2	9.6	26.5
	Experiment 2	5.2	1.5	10.2
	Experiment 3	0.5	3.1	8.8
<i>Maslyanit 12</i>	Experiment 1	0.0	0.72	8.0
	Experiment 2	3.3	17.2	42.4
	Experiment 3	174.0	0.055	3.7

and high ($174 \mu\text{m/h}$) in the other (Table 1). Obviously, this “false wearless” can be explained by the presence of iron minium, which generates a thin film on the friction surface. As is known, iron minium – iron oxide Fe_2O_3 – is used to create the corrosion-resistant and moisture-proof coating of structures. In case of friction in salt water, a thin tear-resistant film is most likely generated on the friction surface.

It should be noted that complex physicochemical changes associated with the development of competing processes of destruction and structuring occur during the formation of the friction transfer film in the surface layer of the polymer body. From the point of view of thermodynamics and structural and energy self-organization, the initial stage of friction (running-in) is characterized by the intensive destruction of the initial structures and formation of new, so-called tribostructures with higher antifriction properties. At the same time, some kind of the self-organization of the tribosystem takes place [18–21, 22].

All three tested materials (Figure 3) have significantly worse results in friction with titanium than in friction with steel and bronze; this is typical for titanium alloys [21, 23]. The antifriction properties of *Maslyanites* during friction with all metal counterbodies are better than that of *Polyamide P-610* (Figures 4–6). In addition, *Polyamide P-610*, within the entire resource of the experimental time (11 hours), when tested in tandem with steel and bronze, is characterized by a constant increase in the friction coefficient instead of its stabilization.

The friction coefficient peak for *Polyamide P-610* (Figure 6) in tandem with a titanium counterbody (increasing to 0.7) is correlated with the wear test results (Figure 3), showing the limit value of the wear rate ($178 \mu\text{m/h}$) for all ex-applications. Destructive processes in the friction zone can explain a sharp decrease in the friction coefficient during its catastrophic wear.

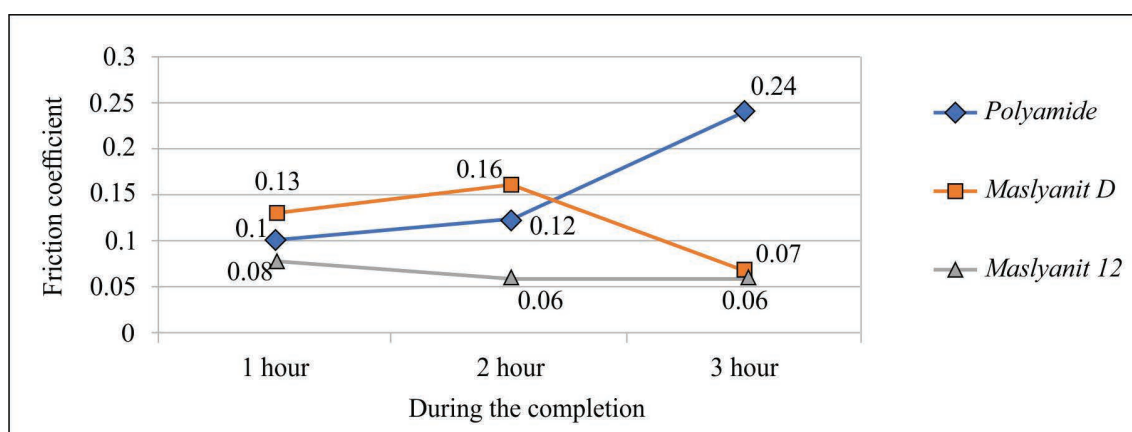


Fig. 4. Dynamics of friction coefficients values of a pair: stainless steel $12\text{Cr}18\text{Ni}9\text{Ti}$ and polymeric material during the completion of the running-in process

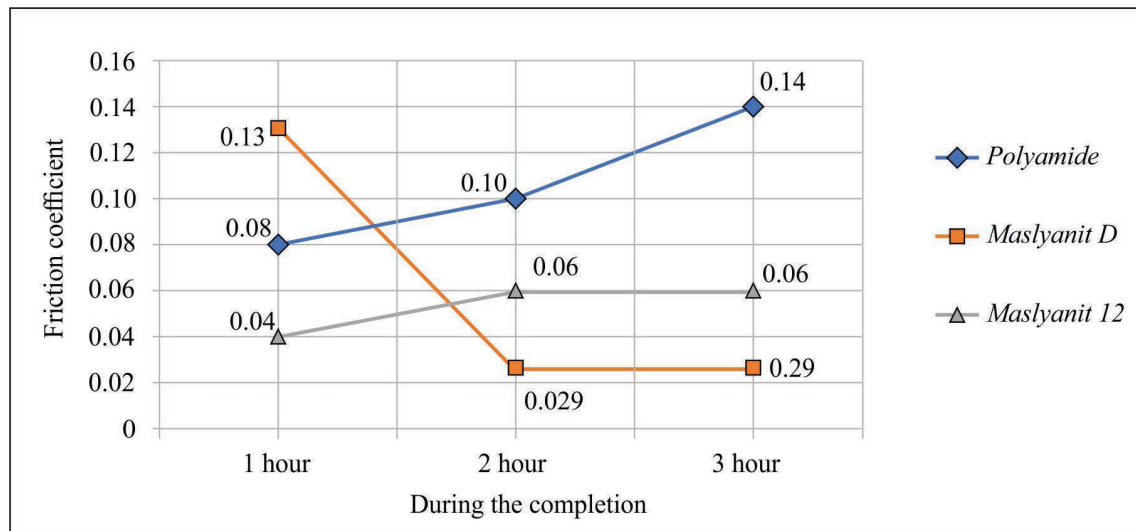


Fig. 5. Dynamics of friction coefficients values of a pair: bronze (9 % Al; 2 % Mn) and polymeric material during the completion of the running-in process

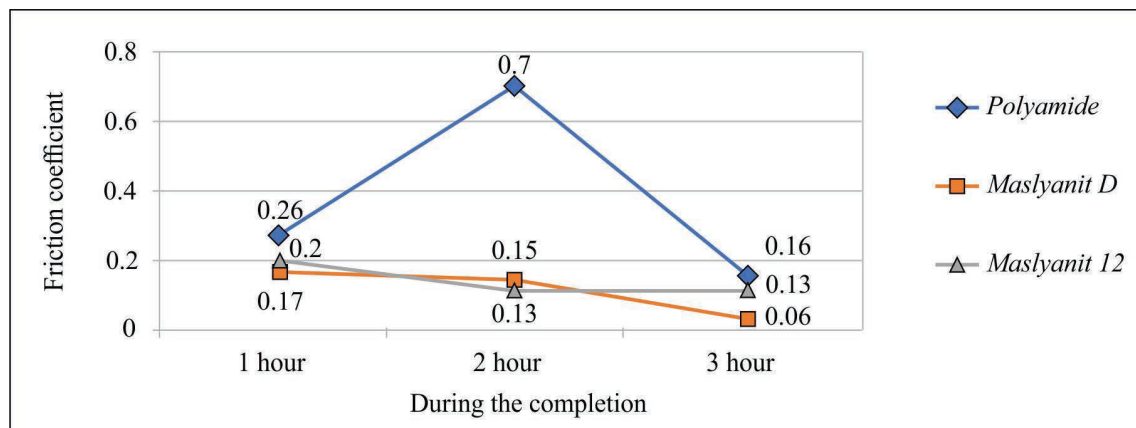


Fig. 6. Dynamics of friction coefficients values of a pair: titanium alloy VT-3 and polymeric material during the completion of the running-in process

In turn, the nature of the running-in process of the metal-polymer friction pair, which largely determines the further life of the working unit of the mechanism, depends on the hardest surface grade of finish [24, 25]. To study the influence of this factor (roughness) on the tribotechnical properties of the metal-polymer pair, bronze (9 % Al; 2 % Mn) and *Maslyanit 12*, the wearless properties of which were of particular interest for further studies, were selected. Bronze counterbodies were made with five different grades of surface finish. Each test was performed according to the above procedure for one hour. The test results are presented in Table 2 and shown graphically (Figure 7–9).

Water, including sea one, which negatively affects the friction of metal pairs, favorably affects the friction process of *Maslyanites*. This is explained by the hydrodynamic effect that occurs in the contact zone in addition to separation oxide film mentioned above.

It should be noted that in units with frequent stops or with the possibility of abrasive getting into it, friction occurs with permanent running-in. This is due to the transition of hydrodynamic friction to boundary friction, which wear is 3–4 times higher than in liquid friction [23].

The graphs of the effect of counterbody surface roughness on hourly mean wear and wear per kilometer of slip path traveled (Figure 7 and 8) are identical and tend to reduce wear as the roughness of the metal surface decreases.

Table 2

**Results of the effect of metal surface roughness on a metal-polymer friction pair operation
in a sea water simulator**

Sequence number	Counterbody roughness parameter – R_a , μm	Mean hourly wear of <i>Maslyanit 12</i> , $\mu\text{m/h}$	Mean wear of <i>Maslyanit 12</i> per 1 km of track, $\mu\text{m/km}$	Friction coefficient
1	3.2	30.6	9.05	0.0450
2	1.6	22.0	6.5	0.0391
3	0.8	20.3	6.0	0.0309
4	0.4	10.0	2.96	0.0236
5	0.2	8.6	2.62	0.0200

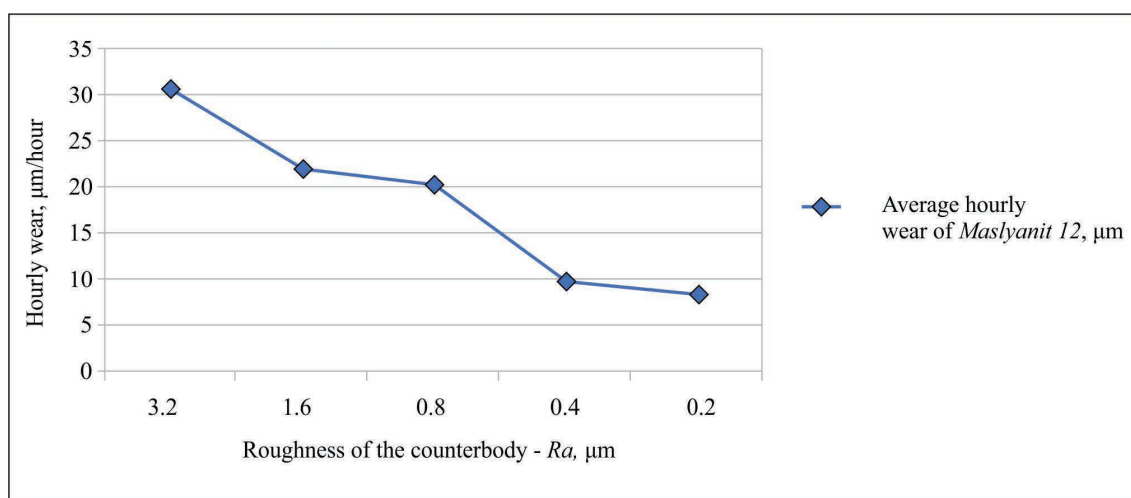


Fig. 7. Influence of the counterbody roughness on the average hourly wear of *Maslyanite 12*

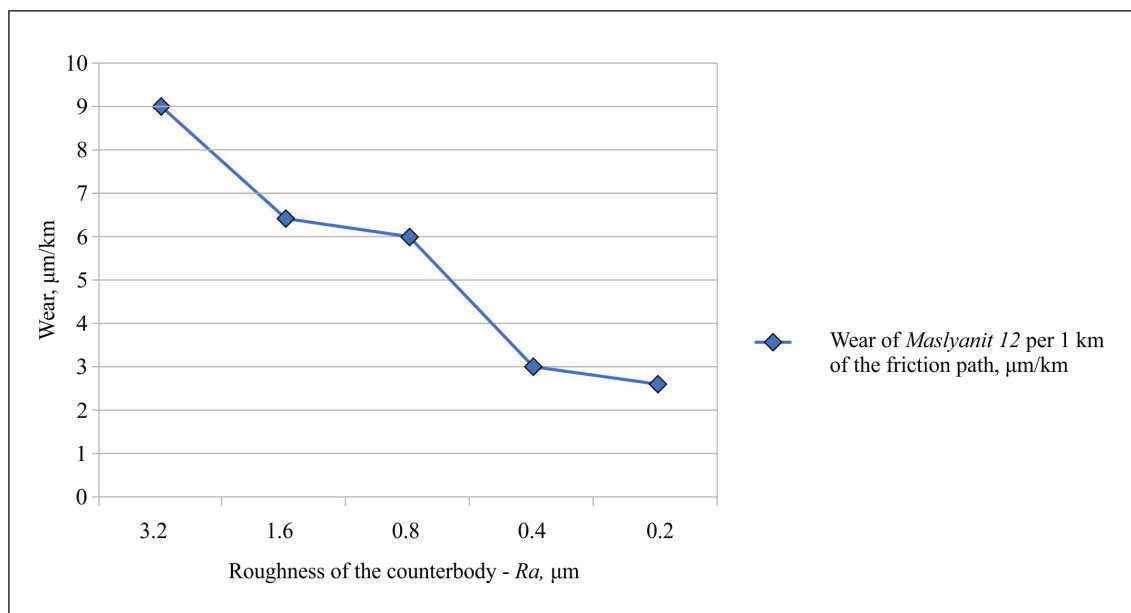


Fig. 8. Influence of the counterbody roughness on the wear of *Maslyanite 12* per 1 km of the friction path

It should be expected that since a surface with a greater roughness, like blades, better captures and tightens the lubricating medium (in our case, the seawater simulator) into the contact gap, it should favor the creation of increased pressure and hydraulic wedge in contact, which ensures the “flotation” of the shaft.

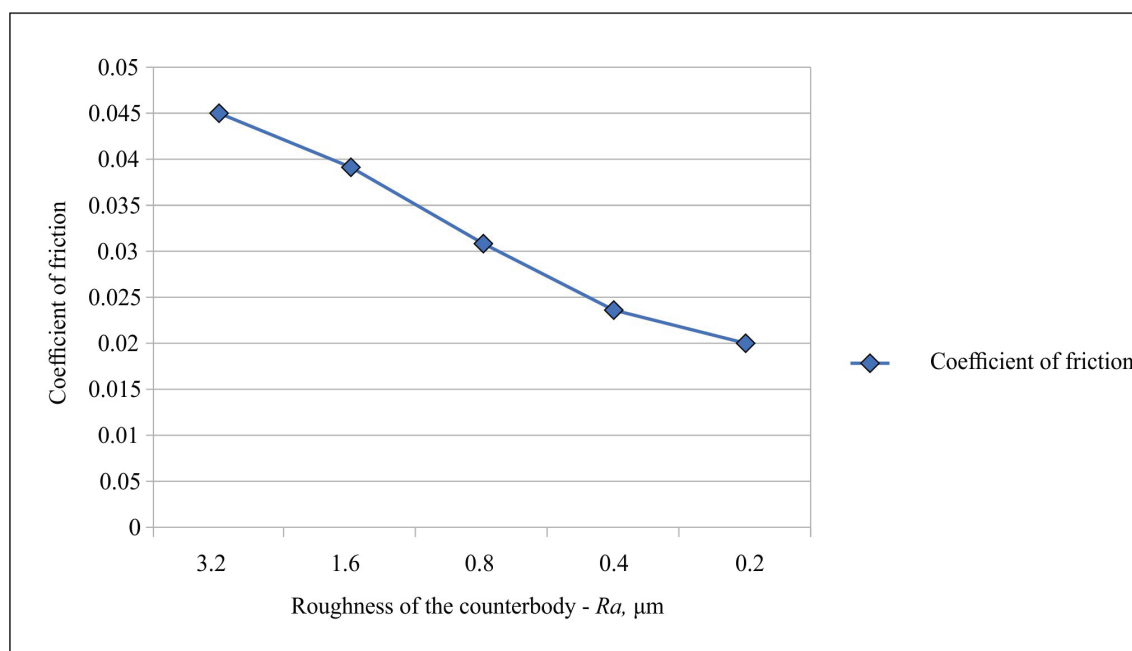


Fig. 9. Influence of the counterbody roughness on the coefficient of friction of *Maslyanyt 12*

However, many factors influence the hydrodynamic friction effect: specific pressure, sliding speed, medium viscosity, etc., the optimum of which is difficult to ensure not only in real practice, but also at the research stage, which is confirmed by these studies. As a result, increased wear of the polymer composition prevails during the running-in and micro running-in period due to the cutting action of the bronze surface microasperities. A film of macromolecules of polyamide, bronze decomposition and iron minium formed in the initial period of friction because of tribodestruction are preserved in the surface deformable layers of the composite and on the working surface of the counterbody. The positive tendency to reduce wear and friction with an increase in the grade of surface finish can be explained by a softer smoothing of the small microasperities of the counterbody, faster running-in, lapping of working surfaces and, therefore, the early steady-state wear process and the “self-organization” of the tribosystem.

Bench tests in seawater

The tests were performed near Sochi (Lazarevskoye).

Since significant heating of the material may occur during friction due to the low thermal conductivity of plastics and heat removal from the friction zone, mainly only through a metal counterbody, and also considering that in addition to the load from the transmitted working force the units of real sea vessels and deep-sea equipment also experience water pressure, it was necessary to conduct tests as close as possible to real operational conditions. A bench of deep-sea field tests was created to conduct these studies. This test bench represented a chamber into which sea water was supplied using a high-pressure pump (up to 200 atm.). Bronze (9 % *Al*; 2 % *Mn*) and *Maslyanit 12* were chosen as friction pair materials for comparison of laboratory and bench results. The test samples were in the form of $\varnothing 80 \times 50 \times 26$ half-liners (Figure 10) and internal grooves to provide continuous access of the lubricant – sea water – to the friction zone. To relieve internal stresses, samples made by injection molding were heat treated in *Vapor* oil. Prior to testing, the samples were kept in sea water for 24 hours. The tests were performed at a specific load of 2.5 MPa and a sliding speed of 0.3 m/s. The measurements were taken every 3 hours during running-in and 50 hours after the steady-state wear. The total duration of the test was 670 hours. Measurement points were marked according to the template.

The period of friction running-in lasted 72 hours, after which the wear rate was set at 0.5–0.8 $\mu\text{m/h}$. As a result of visual inspection and measurements of samples performed at the end of the tests (average wear



Fig. 10. Samples of *Maslyanit 12* after bench tests in sea water

less than 0.5 mm), it was found that there are no traces of tearing, catastrophic wear, melting and other abnormal processes on the friction surfaces. At the same time, wear and tear of the bronze shaft, which was paired with *Maslyanit 12*, was not detected.

Conclusion

The study of the tribotechnical properties of materials based on polyamide in the medium of a sea water simulator made it possible:

- to choose the test materials on the basis of theoretical surveys;
- to develop a test method and experimental equipment;
- to perform laboratory tests of chosen materials. It was revealed that the friction pair bronze (9 % Al; 2 % Mn) and *Maslyanit 12* has high antifriction properties and wear resistance when operating in a sea water simulator; the wear and friction coefficient of the studied friction pair is less than the metal surface grade of finish;
- to verify laboratory test methods in conditions simulating the actual operation modes of the product. It was established that the results of laboratory and bench tests are correlated with each other and allow for the further use of the laboratory test method for the preliminary selection of optimal friction pairs operating in sea water;
- to confirm that wear of filled polyamide composite materials of the *Maslyanit* group in the considered media after the completion of the running-in process occurs mainly by the fatigue mechanism, which is facilitated by the protective film adsorbed on the working surfaces.
- to recommend the selected and studied friction pair for use in various options (shaft-plug, sliding guides, etc.) for bearings, thrust bearings, movable supports and guides of construction, shipbuilding, ship repair industries (port and deck mechanisms, process equipment, floating rigs, high-speed hydrofoil passenger ships, propeller and steering devices, ship centrifugal submersible pumps, equipment for oil production platforms, marine fish farms, desalination and power plants, etc.), which are in contact with fresh or sea water.

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Conflicts of Interest

The authors declare no conflict of interest.

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