ISSN 1068-3666, Journal of Friction and Wear, 2023, Vol. 44, No. 4, pp. 253–258. © Allerton Press, Inc., 2023.
Russian Text © The Author(s), 2023, published in Trenie i Iznos, 2023, Vol. 44, No. 4, pp. 376–384.

Effect of Ion-Plasma Surface Treatment on Tribological Characteristics of Polyurethane

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Received June 28, 2023; revised August 4, 2023; accepted August 10, 2023

Abstract—The aim of this study is an experimental-based analysis of the effect of surface treatment, leading to the formation of carbonized layers, on the coefficient of sliding friction of two polyurethane materials that differ in mechanical and rheological properties. The properties were determined by the results of indentation on a NanoScan-4D scanning nanohardness tester. A ceramic ball with a diameter of 2.1 mm was used as an indenter, which was pressed into the samples at a given linear velocity. The indentation curves at low and high indentation velocities were used to calculate the longitudinal and instantaneous reduced modulus of elasticity. It was found that the longitudinal elastic moduli differ by more than seven times, and the rheological properties of a more rigid material are weak. Tribological tests were performed on a UMT-3 friction machine in the mode of unidirectional sliding friction at a constant load and velocity. Based on the data, regression equations were calculated and the dependences of the friction coefficient on the load and sliding velocity were obtained. The influence of the surface treatment fluence on the surface roughness, adhesion, and deformation friction force is analyzed, data are correlated with the known experimental and theoretical results. It is shown that surface treatment with a relatively small fluence gives fundamentally different effects for the two studied materials: a slight change in roughness and decrease of friction coefficient for the more rigid polyurethane; a significant increase in roughness and a consistently high coefficient of friction, which varies slightly in the considered ranges of loads and velocities. Thus, surface treatment can be used for controlling the coefficient of friction of polyurethane and ensuring its consistently high frictional properties.

Keywords: friction, polyurethane, carbonized layer, indentation, reduced modulus of elasticity, roughness

DOI: 10.3103/S1068366623040098

INTRODUCTION

Polyurethanes are classified as elastomers due to their ability to undergo large deformations and the presence of rheological properties. The use of polyurethane materials in various applications is due to their inherent wide range of different characteristics (including mechanical and tribological), which, in turn, depend on the functional groups they contain (simple, ester, urea, amide, and others). Extrusion and injection molding are the main production processes for structural polyurethane products. In this study, we used polyurethane samples made by injection technology, which is convenient for the manufacturing of products of complex shape and coatings on a rigid base [1]. When manufacturing by varying the ratio of the prepolymer-hardener and temperature regimes, a variety of properties is achieved. The technology of ion-plasma surface treatment, leading to the formation of a nanosized carbonized layer, also affects the characteristics of polyurethane, in particular, roughness [2], mechanical, and rheological properties [3]. These and other parameters affect the friction process. Imperfect elasticity is one of the reasons for the occurrence of resistance during sliding of deformable bodies. Energy dissipation, which occurs when a material is deformed, is a source of friction. Surface properties, in particular roughness, significantly affect the adhesive component of the sliding friction force [4].

The polyurethane materials studied here are primarily attractive for their high coefficient of friction, which is useful for some applications. The most obvious example of the use of a material, where high demands are placed on it in terms of grip, is the sole of a shoe [5]. Similar materials with a different set of characteristics and under completely different friction conditions may already be intended for biomedical use as implants [6].

The technique of ion-plasma treatment of the surface of polyurethane materials [2] was originally developed to improve the biocompatibility of implants, but it also has prospects for use in tribology, since the hard nanolayers formed on the surface have a high degree of adhesion to the base material and also do not change the integral mechanical properties of the material.

Table 1. Surface roughness parameters before and after testing

Specimen	Roughness parameter, nm			
	S_a		R_a	
	initial surface	friction track	initial surface	friction track
No. 1-0	2.7	4.4	4.2	6.6
No. 1-1	2.5	6.2	3.9	10.0
No. 1-2	9.0	21.3	9.8	23.2
No. 2-0	4.4	18.9	6.8	20.5
No. 2-1	12.7	38.5	20.8	22.0
No. 2-2	22.1	68.0	29.7	62.2

Objective—Experimental study and analysis of the influence of surface treatment, leading to the formation of carbonized layers, on the coefficient of sliding friction of two polyurethane materials differing in mechanical and rheological properties.

MATERIALS AND METHODS

The study was carried out on samples of polyurethane materials of two compositions, No. 1 and No. 2, the formulations of which differ in the concentrations of the hardener and prepolymer components. Polyurethanes are made using injection technology, the surface of which was treated with nitrogen ions with an energy of 20 keV at different exposure times corresponding to a fluence of 10^{15} (samples No. 1-1 and No. 2-1) and 10^{16} (samples No. 1-2 and No. 2-2) ions/cm^2 [12]. To compare and determine the mechanical characteristics (elastic modulus), samples without surface treatment were also used (samples No. 1-0 and No. 2-0).

The elastic modulus was calculated using experimental data obtained by instrumental indentation using a NanoScan-4D scanning nanohardness tester (TISNUM, Russia). This technique makes it possible to obtain the dependence of the load on the depth of penetration of the rigid tip into the material under study during loading and unloading. In this study, a ceramic (Al_2O_3) ball with a diameter of 2.1 mm, which was pressed into the samples at a given linear speed. Since the modulus of elasticity for a viscoelastic material is not a constant, for indentation we used penetration rates close to the maximum and minimum values allowed by the device: 1000 mN/s and 4 mN/s. At the same time, maintaining the speed for different types of materials was achieved by varying the load and time during testing. In this case, the exposure time under maximum load (before the unloading process) did not change and was 2 s. For material No. 1-0, a load of up to 1000 mN was carried out in 1 s, and for material No. 2-0, up to 200 mN in 0.2 s; in another case, up to 1000 mN in 250 s and up to 200 mN in 50 s, respectively. For each speed/material, three repetitions were performed.

Tribological tests were carried out on a UMT-3 friction machine (Cetr, United States) in the unidirectional friction mode when a rigid ceramic ball with a diameter of 1.5 mm slid along the surface of the materials under study at constant load and speed. The experiments were carried out in accordance with the methodology of a two-factor planned experiment [8]. The desired dependence of the friction coefficient was found on the basis of a series of tests, in which the limits of load change (from 5 to 100 g) and sliding speed (from 0.1 to 1 mm/s) were set at three levels: minimum, average, and maximum. For each selected combination of parameters, the experiment was repeated three times. In order to reduce the influence of random factors on the dependence under study, the sequence of tests was chosen randomly. Based on the data obtained, regression equations were calculated and the dependence of the friction coefficient on the load and sliding speed was plotted. Figure 3 shows isolines of the friction coefficient for all six materials under study.

For non-destructive and fast assessment of surface nanogeometry, a noncontact optical 3D profilometer S neox (SENSOFAR-TECH, Spain) was used, equipped with 5X, 20X, and 150X confocal objectives and a motorized object stage for obtaining images from large areas by stitching several images. Table 1 presents the surface roughness parameters of all studied materials before and after tribological tests. The surface roughness of the friction tracks is given only for qualitative comparison with the original surface since the values were obtained with the missing length of the base segment to obtain a reliable value of the roughness parameters according to the standard. Friction paths corresponding to maximum load values and minimum speed were studied.

RESULTS AND DISCUSSION

Figure 1 demonstrates good repeatability and convergence of results in the experimental load-indentation depth diagram. Figure 2 shows the effect of indentation speed on the loading and unloading curves

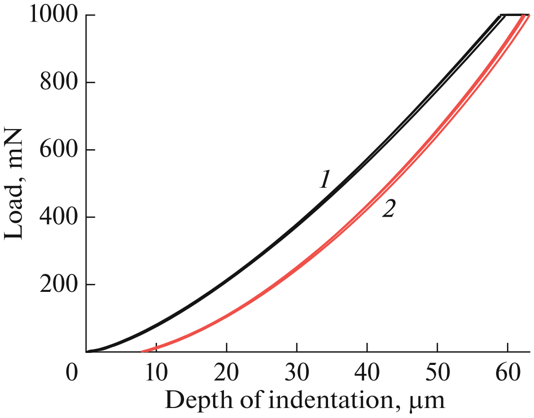

Fig. 1. Loading (*1*) and unloading (*2*) curves of load-penetration dependence for material 1-0 at an indentation velocity of 1000 mN/s (3 tests).

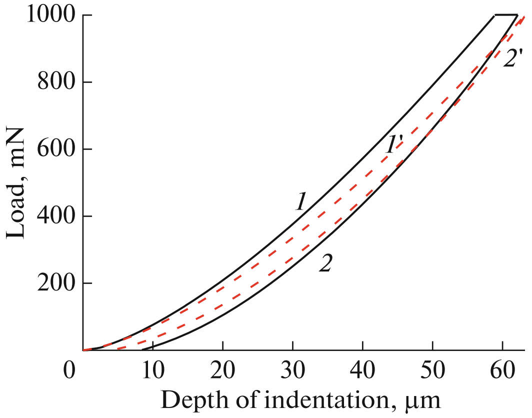

Fig. 2. Comparison of load-penetration dependences during loading (curves *1*, *1*') and unloading (curves *2*, *2*') for material 1-0 at indentation velocities of 1000 mN/s (solid lines) and 4 mN/s (dashed lines).

using material No. 1-0 as an example. For material No. 2-0, a similar behavior is observed, but with a more significant divergence of the curves at different speeds, which indicates that the rheological properties of this material are more pronounced.

The indentation curves at low and high indentation velocities were used to calculate the long-term and instantaneous reduced modulus of elasticity based on relationship [7]:

$$d^{3/2} = \frac{3P}{4\sqrt{R}E^*}, \quad E^* = \frac{E}{1-\nu^2}. \tag{1}$$

Calculated instantaneous and long-term reduced moduli of elasticity E^* for material No. 1-0 were 52.5 and 45.9 MPa, for material No. 2-0, 8.8 and 6.1 MPa, respectively. Thus, the first material is practically elastic, while the second is viscoelastic and significantly more pliable.

Carbonized layers formed as a result of surface treatment are relatively hard and not always continuous [2, 3]. The greater the fluence, the greater the rigidity of the nanosized surface layers.

Data on the viscoelastic properties of materials, combined with information on surface microgeometry and surface treatment conditions, provide sufficient information to analyze and explain the results presented in Fig. 3.

It is known that under normal conditions, roughness reduces or even makes adhesion forces between surfaces negligible due to the discreteness of contact, since adhesion forces depend on the area of actual contact. The adhesion interaction of rough surfaces was studied in [9], where it was shown that an increase in roughness leads to a significant decrease in adhesion forces. In this case, each protrusion was considered in isolation from the others, and their mutual influence and the possibility of transition to saturated contact were not taken into account. However, experiments conducted on highly elastic and polymeric materials [10] showed that with a gradual increase in roughness, the forces of adhesion and adhesive friction first increase compared to the case of a smooth surface, and only then decrease. Thus, the maximum value of the adhesion force is achieved not for a smooth surface, but for some, relatively small, roughness. This is explained by the fact that for a smooth surface, the contact is continuous, and with a small increase in roughness, the continuity of the contact is maintained (provided that the material is sufficiently soft and the surface energy is sufficiently high), while the effective contact area increases. With a further increase in roughness, the contact becomes discrete, and the adhesive attraction decreases. The solution to the contact problem for an indenter and a half-space with a small waviness applied to one of the surfaces, when the contact area remains simply connected, was obtained analytically [11]. It has been established that, under conditions of continuous contact, the application of a relief increases the effective adhesive properties of the surface, as well as the magnitude of adhesive hysteresis [12], which correlates with the magnitude of the adhesive friction force.

Material No. 1-0 is practically elastic; the deformation component of the friction force in this case may not be taken into account. All three samples of the material, regardless of surface treatment, demonstrate the independence of the friction coefficient from speed in the studied range of loads and speeds (Figs. 3a, 3c, and 3e). Since polyurethane materials have significant surface energy, it must be assumed that adhesion is the main cause of frictional forces. If the surface roughness is relatively small (which is the case for samples No. 1-0 and No. 1-1, without surface treatment and with low-fluence treatment), the contact remains continuous, and the friction force due to the adhesive interaction does not depend on the load,

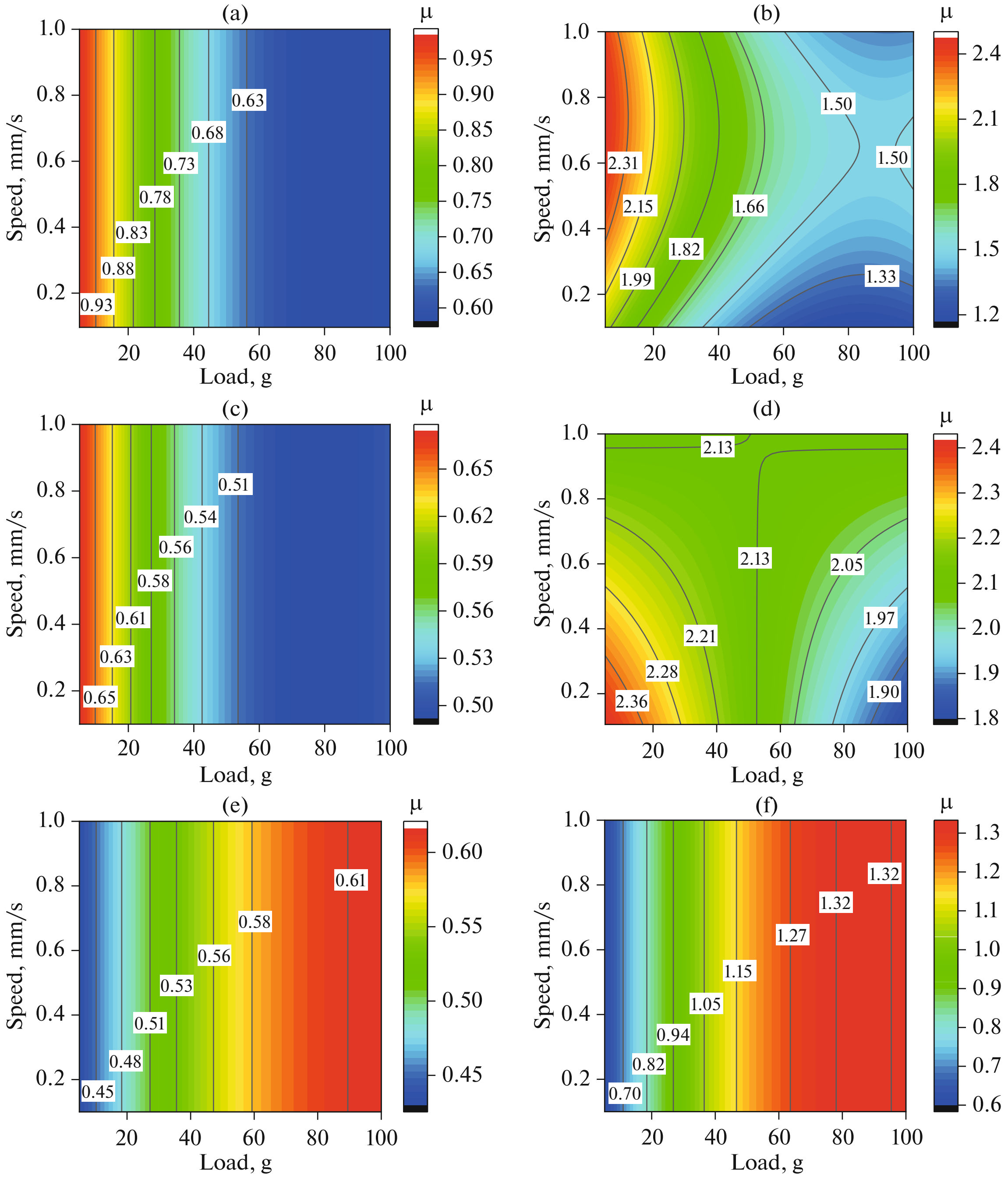

Fig. 3. Isolines of friction coefficient μ for material 1-0 (a), material 1-1 (c), material 1-2 (e), material 2-0 (b), material 2-1 (d), material 2-2 (f).

this was shown for the case of regular sinusoidal roughness in [13]. In this case, the coefficient of friction, which is the ratio of the friction force to the load, will be inversely proportional to the load (Figs. 3a, 3c, and 3e). The difference in the absolute values of the friction coefficient for samples No. 1-0 and No. 1-1 is probably due to a change in surface energy due to the formation of nanosized carbonized layers that partially screen adhesion. With an increase in roughness, the contact becomes discrete, in this case, the actual contact area and both components of the friction force increase rapidly with increasing load [13], as a result, the dependence of the friction coefficient on the load increases, as happens in the case of material No. 1-2, where the surface fluence processing 10^{16} ions/cm^2 leads to a significant, more than threefold, increase in roughness. It can be assumed that for some intermediate roughness values this dependence will be close to a constant in the range under study.

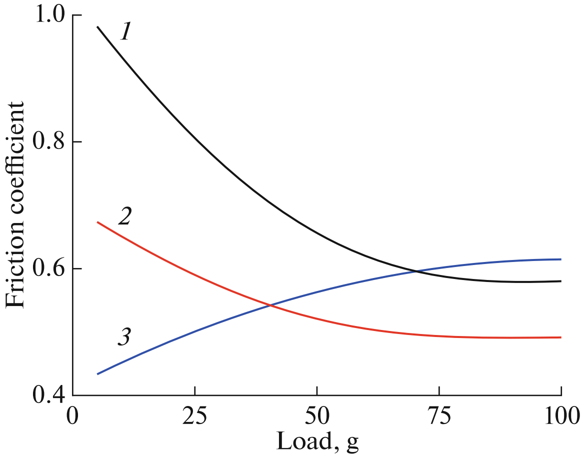

Fig. 4. Dependence of the friction coefficient on the load for material 1-0 without surface treatment (curve *1*), material 1-1 with a layer of fluence 10^{15} (curve *2*), material 1-2 with fluence 10^{16} (curve *3*).

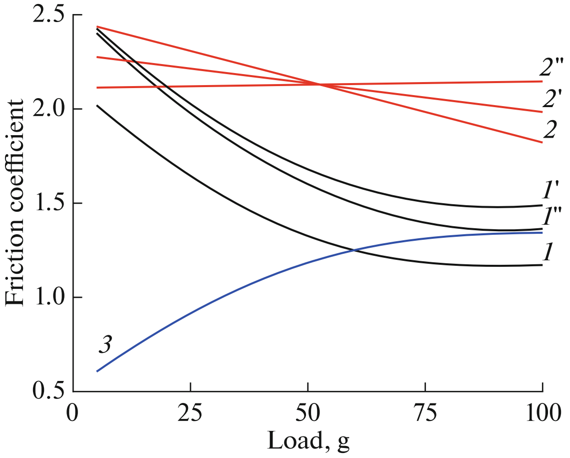

Fig. 5. Dependence of the coefficient of friction on the load at a fixed velocity of 0.1 mm/s (curves *1*, *2*), 0.55 mm/s (curves *1*', *2*') and 1 mm/s (curves *1*'', *2*'') for material 2-0 without surface treatment (curves *1*, *1*', *1*''), material 2-1 with fluence 10^{15} (curves *2*, *2*', *2*''), material 2-2 with a fluence 10^{16} (curve *3*).

In the case of a viscoelastic material, the friction force is significantly affected by its deformation component, which manifests itself in the dependence of the friction force on speed. Study [14] is devoted to the experimental study and modeling of the deformation component of the friction force for rubber using a technique that levels out adhesion forces, where it is shown that there is an indenter sliding speed at which the deformation component of the friction force reaches a maximum; the speed value depends on the load. Isolines in Fig. 3b (material No. 2-0 without surface treatment and with low roughness) correspond to a combination of adhesive, decreasing with increasing load, friction force, and deformation component, demonstrating a nonmonotonic dependence on speed. The speed providing the maximum value of the deformation component at a fixed value of the load drops slightly with increasing load. The presence of a rigid surface layer reduces the deformation component of the friction force [3, 15]. In our case, this effect can be traced for material no. 2-2 processed with a large fluence, for which there is no dependence of the friction coefficient on speed, and the load effect corresponds to the variant of relatively high roughness, similar to the effect obtained for material No. 1-2, processed with the same fluence. For material No. 2-1, the surface of which was treated with a low fluence, a significant, almost threefold, increase in roughness was obtained. It can be assumed that in this case the carbonized layer is not continuous and has little effect on the adhesive forces, and also does not reduce the deformation component of the friction force. As a result, the dependence of the friction coefficient on the load at low speed is characteristic of continuous contact (i.e., a decrease in the friction coefficient with increasing load), and at high speeds this dependence is smoothed out due to the floating effect for a viscoelastic material at a high sliding speed [12], leading to the discreteness of contact.

The roughness of the friction paths in all cases is greater than the roughness of the initial surface, its change is more significant for materials No. 2-0, No. 2-1, and No. 2-2, which demonstrate less large values of the friction coefficient compared to the first group of materials. However, the roughness remains at the nanoscale.

Figures 4 and 5 show the dependences of the friction coefficient on the load at a fixed speed for materials of the first (Fig. 4) and second (Fig. 5) groups. Materials for which there is no dependence on speed are represented by one line, otherwise the speed is fixed at three values.

These results allow us to analyze the influence of surface treatment on the friction coefficient values. For the first group of materials, surface treatment, in general, leads to a decrease in surface energy and adhesion forces due to the appearance of carbonized layers. The exception is material No. 1-2 at high load values, when the friction coefficient is slightly higher than that recorded for the untreated material at the same parameter values. The most interesting result presented in Fig. 5 is the consistently high value of the friction coefficient obtained for material No. 2-1, which varies slightly in the studied load and speed ranges (from 1.82 to 2.44).

CONCLUSIONS

The influence of surface modification (treatment with nitrogen ions with an energy of 20 keV at various fluences that differ by ten times) on the change in the surface microgeometry and frictional properties of two polyurethane materials obtained by injection technology has been studied. The indentation results showed that the materials differ significantly in stiffness and rheological properties.

It has been established that the friction forces arising when a ceramic ball slides over the polyurethane surface are of an adhesive nature, and also, in the case of a material with pronounced viscoelastic properties, a deformation component of the friction force is added. Surface treatment leads to the appearance of relatively hard nanosized carbonized surface layers, which, in the case of high fluence, reduce the surface energy responsible for adhesion forces, and also completely neutralize the deformation component of the friction force. Processing with a relatively small fluence gives fundamentally different effects for the two studied materials: a slight change in roughness and a drop in the friction coefficient for more rigid polyurethane; a significant increase in roughness and a consistently high coefficient of friction, which varies slightly in the considered ranges of loads and speeds.

Thus, surface treatment can be used as a means of controlling the coefficient of friction of polyurethane and ensuring its consistently high friction properties.

NOTATION

d	penetration, m
P	load, N
R	ball radius, m
E^*	reduced modulus of elasticity, Pa
E	modulus of elasticity, Pa
ν	Poisson's ratio
μ	coefficient of friction
S_a	arithmetic mean area roughness
R_a	arithmetic mean profile deviation

FUNDING

This study was supported by the Russian Science Foundation, project no. 18-19-00574.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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