ISSN 1068-3666, Journal of Friction and Wear, 2015, Vol. 36, No. 6, pp. 502–508. © Allerton Press, Inc., 2015.
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Mechanical and Tribological Characteristics of Nano- and Microcomposites with UHMWPE–PTFE Polymer–Polymer Matrix

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Received March 5, 2015

Abstract—In order to develop antifriction materials produced by extrusion, the mechanical and tribological characteristics of nano- and microcomposites with a hybrid ultrahigh molecular weight polyethylene (UHMWPE)–polytetrafluoroethylene (PTFE) matrix have been studied under the conditions of dry friction, boundary lubrication, and abrasive wear. Under the conditions of dry sliding friction, using the UHMWPE + 10 wt % PTFE matrix reduces the wear rate of the nano- and microcomposites by 10–30%; the mechanical characteristics of the microcomposites decrease substantially, while those of the nanocomposites diminish only slightly. Under boundary lubrication with distilled water, a similar effect of the size of the fillers on the wear resistance of the composites is observed. During abrasive wear, the wear resistance of the microcomposites significantly exceeds that of the UHMWPE + 10 wt % PTFE matrix, while the introduction of the nanosized fillers into the matrix changes its wear resistance only slightly. The supramolecular structure, the degree of crystallinity, and the topography of the worn surfaces of the developed materials are studied using scanning electron microscopy, differential scanning calorimetry, and light microscopy, as well as the mechanisms of the wear of these materials under the conditions of dry sliding friction and abrasive wear are discussed.

Keywords: antifriction composites, polymer–polymer matrix, ultrahigh molecular weight polyethylene, polytetrafluoroethylene, wear resistance, coefficient of friction, supramolecular structure, transfer film

DOI: 10.3103/S1068366615060124

INTRODUCTION

The introduction of modifiers, which play the role of a solid lubricant, into polymer materials is known to be an efficient way to enhance the tribological performance of these materials [1–9]. In our work [10] devoted to the development of the UHMWPE–PTFE polymer–polymer matrix, the role of the solid-lubricating component was played by fluoroplastic-4, which had a low shear resistance, weak adhesion to metals, the ability to produce transfer films, and the lowest coefficient of friction compared to other commercial polymer-based materials. Under the conditions of dry sliding friction and lubrication, the wear resistance of UHMWPE increased several times, and the maximum increase in the wear resistance (by up to five times) was exhibited by the UHMWPE + 10 wt % PTFE composition.

We believe that it is reasonable to use the above-mentioned hybrid polymer matrix to develop extrudable antifriction nano- and microcomposites for friction units.

The aim of this work was to develop extrudable antifriction composites with the hybrid UHMWPE + 10 wt % PTFE polymer matrix.

EXPERIMENTAL

In order to determine the wear resistance of the composites under conditions of dry friction, boundary lubrication, and abrasive wear, we used Ticona (GUR-2122) UHMWPE powder with a molecular weight of 4.0 million and a particle size of 5–15 μm, F-4PN$_{20}$ fluoroplastic powder with a particle diameter of 14 μm and F-4(PN) fluoroplastic powder with a particle

Physicomechanical characteristics and coefficient of friction of matrix material and composites based on UHMWPE and PTFE

Concentration of filler, wt %	Density ρ, g/cm^3	Shore hardness *D*	Ultimate strength σ_u, MPa	Relative elongation to fracture ε, %	Degree of crystallinity χ, %	Coefficient of friction *f*	
						dry friction	water lubrication
UHMWPE	0.92	59.5 ± 0.6	32.3 ± 0.9	485 ± 23.6	56.5	0.120	0.079
UHMWPE + 10% PTFE	1.00	59.6 ± 0.6	27.0 ± 1.2	428 ± 25.1	41.6	0.089	0.067
0.5 AlO(OH) nanosized	1.00	58.3 ± 0.5	29.7 ± 1.2	439 ± 23.5	40.5	0.099	0.067
0.5 SiO_2 nanosized	1.00	58.6 ± 0.4	28.8 ± 0.9	409 ± 19.5	42.3	0.098	0.068
0.5 UNV nanosized	1.00	58.5 ± 0.6	28.2 ± 1.2	400 ± 22.1	42.1	0.096	0.067
20 Al_2O_3 microsized	1.14	61.2 ± 0.6	22.7 ± 1.3	296 ± 14.9	29.2	0.118	0.095
20 AlO(OH) microsized	1.16	60.5 ± 0.7	24.2 ± 1.3	333 ± 20.1	30.5	0.101	0.078

diameter of 100–180 μm, UNV carbon nanofibers 60 nm in diameter and AlO(OH) nanofibers 10 nm in diameter, and 90–100-nm SiO_2 nanoparticles, as well as 2–3-μm AlO(OH) and 50-μm Al_2O_3 microparticles. Specimens of the polymer composites were produced by hot molding under a pressure of 10 MPa at a temperature of 200°C, followed by cooling with a rate of 4°C/min. Mixtures of the UHMWPE and PTFE powders, as well as the powders of the fillers, were agitated using an MP/0.5*4 planetary-type ball mill involving the preliminary dispersion of the components using an ultrasonic bath.

The wear resistance of the materials under the conditions of dry friction was determined using the block-on-ring arrangement implemented in an SMT-1 friction machine in accordance with the standard ASTM G99 under a load applied to the specimen of 68.8 N and at the velocity of rotation of the shaft of 100 rpm, which corresponded to the velocity of sliding of 0.32 m/s. The specimens were 7 × 7 × 10 mm in size (H × W × D). The ShKh15 steel counterbody was 62 mm in diameter. The friction surfaces of the specimens were examined using a Zygo New View 6200 optical profilometer. The area of the friction track was determined using the Rhino Ceros 3.0 software package by manually selecting the contour of the worn surface (friction track), then automatically calculating its area.

The specific pressure during the extrusion of the powder mixtures was assessed using a UE-MSL plunger (piston) laboratory extruder (Great Britain). The abrasive wear tests were carried out using am MI-2 tribometer for testing rubbers for abradability. The wear resistance was determined under a load of 0.15 MPa at a velocity of the sliding of the shaft relative to a pair of the specimens of 17.0 m/min. Particles of R240 abrasive (GOST 426) with a grain size of 58.5 μm fixed to a paper substrate were used. The volume abrasive wear was determined by weighing the specimens, followed by calculating the mass loss every 5 min. The test method complied with the requirements of the standards ASTMG99 and DIN 50324. The tribological characteristics were determined by averaging the results obtained for four specimens.

The structural examinations were carried out in a LEOEVO 50 scanning electron microscope at an accelerating voltage of 20 kV using the fracture surfaces of the notched specimens, which were mechanically fractured after exposure in liquid nitrogen. The degree of crystallinity was determined using an STD Q600 differential scanning calorimeter and IR spectra were recorded using a NIKOLET 5700 spectrometer. The mechanical characteristics of the materials were determined in accordance with GOST 11262–80 in the tensile tests carried out using an Instron 5582 testing machine; no less than five dumbbell specimens of each material were tested.

RESULTS AND DISCUSSION

The table presents the tribomechanical characteristics of pure UHMWPE, the UHMWPE + 10 wt % PTFE matrix, and composites based on this hybrid matrix.

The data given in the table show that the Shore hardness *D* of the nanocomposites based on the UHMWPE + 10 wt % PTFE mixture decreases only slightly compared to that of the matrix material (pure UHMWPE), while the Shore hardness of the microcomposites based on this hybrid matrix increases. The ultimate strength and the relative elongation upon the rupture of the nanocomposites decrease only slightly, while filling the matrix with much larger Al_2O_3 and AlO(OH) microparticles leads to a noticeable decrease in these characteristics. The filling of the hybrid matrix with the microparticles causes a significant increase in its density, while the density of the matrix filled with the nanoparticles remains unchanged. The degree of crystallinity of the nanocomposites does not change substantially compared to that of the matrix, but it decreases significantly for the microcomposites.

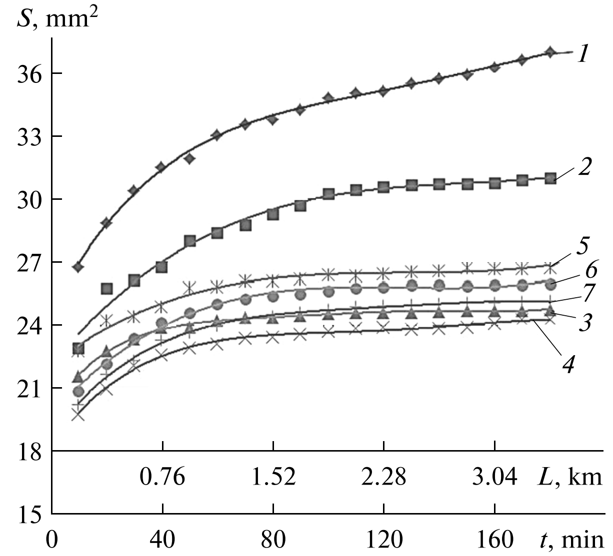

Fig. 1. Kinetic curves for UHMWPE and composites based on UHMWPE–PTFE: (*1*) unfilled UHMWPE; (*2*) UHMWPE + 10 wt % PTFE; (*3*) UHMWPE + 10 wt % PTFE + 0.5 wt % AlO(OH); (*4*) UHMWPE + 10 wt % PTFE + 0.5 wt % SiO_2; (*5*) UHMWPE + 10 wt % PTFE + 0.5 wt % UNV; (*6*) UHMWPE + 10 wt % PTFE + 20 wt % Al_2O_3; (*7*) UHMWPE + 10 wt % PTFE + 20 wt % AlO(OH). Particle size of PTFE powder is 14 μm.

Dry Sliding Friction

An analysis of the kinetic curves of the wear of UHMWPE, the hybrid UHMWPE + 10 wt % PTFE matrix, and the composites based on this matrix (Fig. 1) has shown that the wear rate of the composites is less than that of unfilled UHMWPE and is less than that of the hybrid matrix. Figure 2 shows the steady wear rate diagram (I, mm^2/min) for the composites that contain fillers with different degrees of fineness. Note that the wear rate of the composites based on the UHMWPE–PTFE matrix depends only slightly on both the concentration and the particle size of the filler and varies in the range of 10–35% depending on the type of the filler. It can be seen that the nanosized fillers are more efficient (bars *3*–*5*), while using the AlO(OH) microparticles increases the wear resistance of the composites by only 10% as compared to that of the matrix. The roughness of the friction surfaces of all the composites depends on the type of the filler in a similar manner (Fig. 2).

Thus, despite the noticeable decrease in the ultimate strength of the microcomposites with the hybrid matrix, the wear resistance of these microcomposites exceeds that of original UHMWPE and is comparable to that of the nanocomposites. This is also confirmed by the values of the coefficient of friction of the materials under study (table). The IR spectra of the microcomposites with the hybrid UHMWPE + 10 wt % PTFE matrix are indicative of the absence of chemical bonds between the fillers and the components of the mixtures.

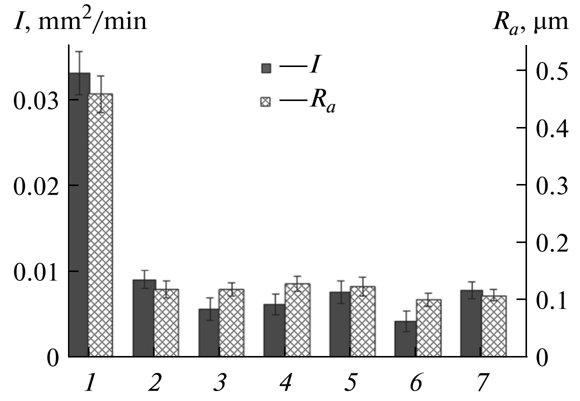

Fig. 2. Wear rate (*I*) and roughness of friction surfaces (R_a) of UHMWPE and composites based on UHMWPE–PTFE at steady wear stage: (*1*) unfilled UHMWPE; (*2*) UHMWPE + 10 wt % PTFE; (*3*) UHMWPE + 10 wt % PTFE + 0.5 wt % AlO(OH); (*4*) UHMWPE + 10 wt % PTFE + 0.5 wt % SiO_2; (*5*) UHMWPE + 10 wt % PTFE + 0.5 wt % UNV; (*6*) UHMWPE + 10 wt % PTFE + 20 wt % Al_2O_3; (*7*) UHMWPE + 10 wt % PTFE + 20 wt % AlO(OH).

In order to determine the relationship between the structure of the composites, the type of the filler, and the mode of wear during dry sliding friction under the steady conditions, the friction surfaces of the specimens and the supramolecular structure of the composites with the UHMWPE + 10 wt % PTFE hybrid matrix and the fillers with various particle sizes were examined (Fig. 3). The data presented in Fig. 3 show that the filling of the hybrid matrix with the nanosized particles does not lead to transformations of the supramolecular structure (Figs. 3b, 3c), while the microsized fillers hamper the formation of spherulites (Fig. 3d), which is also confirmed by the data on the degree of crystallinity (table). On the other hand, the use of the microsized fillers substantially increases the coefficient of friction of the hybrid matrix, while the use of the nanosized particles has no or little effect on this parameter (table). Unlike matrix UHMWPE, the lubricity of the nanosized fillers in the hybrid matrix is leveled by the effect of the transfer of a PTFE film on the counterface, which primarily governs the tribological characteristics of the material [10].

A different situation is observed for composites with the hybrid matrix containing coarse fluoroplastic particles (180 μm). The nanosized fillers substantially reduce the wear of the composites as compared with that of the original hybrid matrix, thus playing a role of a solid lubricant (Fig. 4, bars *5*–*7*). The contribution of the microsized fillers to the wear resistance of the composites with the hybrid matrix is determined by the particle size of the filler (bars *3* and *4*). The examination of the worn surfaces of the composites with the hybrid matrix containing the coarse fluoroplastic par-

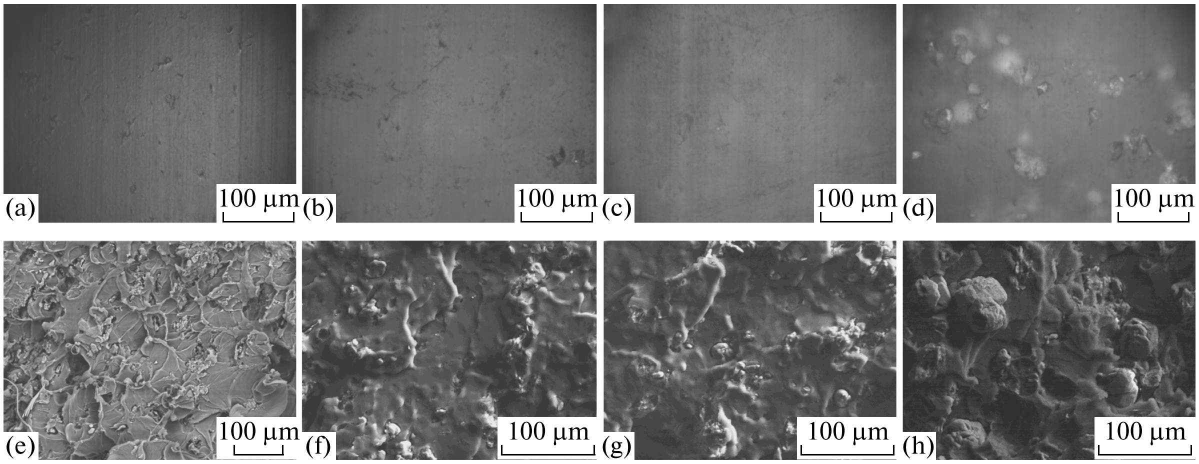

Fig. 3. Microphotos of worn surfaces and supramolecular structure of (a, e) UHMWPE + 10 wt % PTFE; (b, f) UHMWPE + 10 wt % PTFE + 0.5 wt % AlO(OH); (c, g) UHMWPE + 10 wt % PTFE + 0.5 wt % UNV; and (d, h) UHMWPE + 10 wt % PTFE + 20 wt % Al_2O_3 after dry sliding friction. Particle size of PTFE powder is 14 μm.

ticles shows that microgrooves appear on the surface of the matrix, while practically no microgrooves are observed on the worn surfaces of the composites with the UHMWPE + 10 wt % PTFE matrix, which correlates with the data on the wear rate (Fig. 4).

Boundary Lubrication

The results of the tribotests carried out under the conditions of boundary lubrication show that the lubrication properties of PTFE are completely retained. Figure 5 presents the data on the wear rate of the composites with the hybrid matrix and on the roughness of their worn surfaces obtained during friction in distilled water. It can be seen from these data that, under the conditions of boundary lubrication, the wear rate of the composites containing fine fluoroplastic is close to that of the UHMWPE + 10 wt % PTFE matrix. The roughness of the worn surfaces of the composites R_a under lubrication is also close to that of the surface of the matrix, which confirms the governing role of the transfer of the PTFE film on the counterface in the formation of the tribological properties of the composites with the hybrid matrix.

If the hybrid UHMWPE + 10 wt % PTFE matrix contains the coarser fluoroplastic particles (180 μm), the role of the fillers under boundary lubrication is

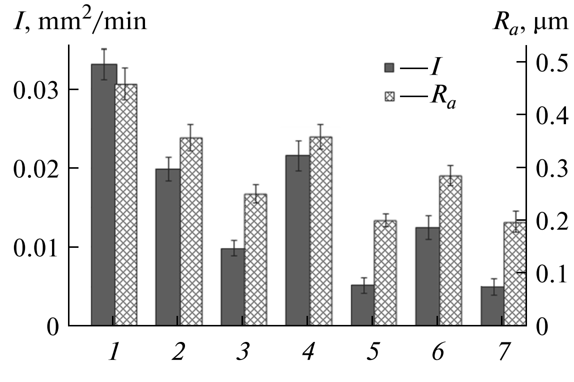

Fig. 4. Wear rate (*I*) and roughness of friction surfaces (R_a) of UHMWPE and composites based on UHMWPE–PTFE at steady wear stage under conditions of dry sliding friction: (*1*) unfilled UHMWPE; (*2*) UHMWPE + 10 wt % PTFE; (*3*) UHMWPE + 10 wt % PTFE + 20 wt % Al_2O_3; (*4*) UHMWPE + 10 wt % PTFE + 20 wt % AlO(OH); (*5*) UHMWPE + 10 wt % PTFE + 0.5 wt % AlO(OH); (*6*) UHMWPE + 10 wt % PTFE + 0.5 wt % SiO_2; (*7*) UHMWPE + 10 wt % PTFE + 0.5 wt % UNV. Particle size of fluoroplastic is 180 μm.

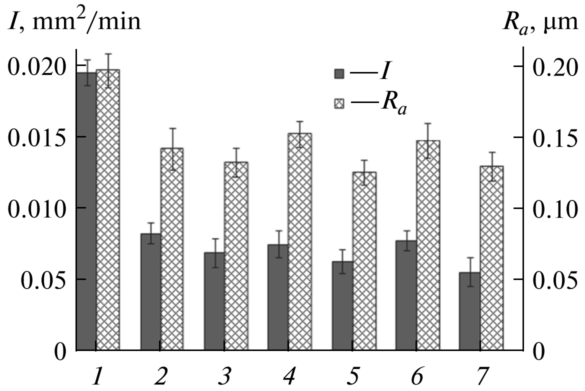

Fig. 5. Wear rate (*I*) and roughness of friction surfaces (R_a) of UHMWPE and composites based on UHMWPE–PTFE at steady wear stage under conditions of boundary lubrication with distilled water: (*1*) unfilled UHMWPE; (*2*) UHMWPE + 10 wt % PTFE; (*3*) UHMWPE + 10 wt % PTFE + 0.5 wt % AlO(OH); (*4*) UHMWPE + 10 wt % PTFE + 0.5 wt % SiO_2; (*5*) UHMWPE + 10 wt % PTFE + 0.5 wt % UNV; (*6*) UHMWPE + 10 wt % PTFE + 20 wt % Al_2O_3; (*7*) UHMWPE + 10 wt % PTFE + 20 wt % AlO(OH). Particle size of fluoroplastic is 14 μm.

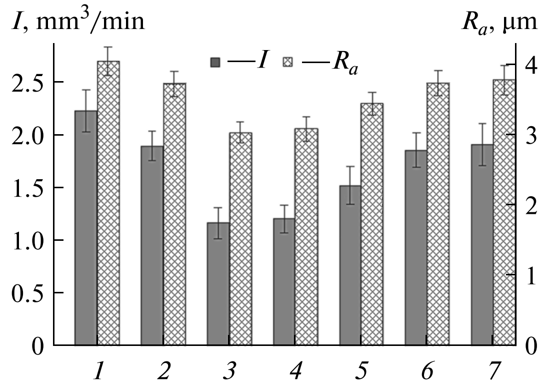

Fig. 6. Wear rate (I) and roughness of friction surfaces (R_a) of UHMWPE and composites based on UHMWPE–PTFE at steady abrasive wear stage: (*1*) unfilled UHMWPE; (*2*) UHMWPE + 10 wt % PTFE; (*3*) UHMWPE + 10 wt % PTFE + 20 wt % Al_2O_3; (*4*) UHMWPE + 10 wt % PTFE + 20 wt % AlO(OH); (*5*) UHMWPE + 10 wt % PTFE + 0.5 wt % AlO(OH); (*6*) UHMWPE + 10 wt % PTFE + 0.5 wt % SiO_2; and (*7*) UHMWPE + 10 wt % PTFE + 0.5 wt % UNV. Abrasive R240. The particle size of fluoroplastic is 14 μm.

reduced to decreasing the wear rate of the composites by 50–70%.

We believe that, in the presence of fine fluoroplastic uniformly distributed in the matrix, a homogeneous transfer film of a stable thickness is quickly formed on the counterface, which ensures the high wear resistance of the composites under the conditions of both dry friction and lubrication.

The presence of the coarse fluoroplastic particles in the matrix in the same volume concentration appears as the nonuniformity of the thickness and even the discontinuity of the transfer film on the counterface. In this case, the nanosized fillers entirely complete the function of the solid lubricant under the conditions of dry friction and lubrication, and the coefficient of friction properly reflects the state of the friction surfaces (table).

Abrasive Wear

Figure 6 shows the abrasive wear rate diagram for all the composites with the hybrid UHMWPE + 10 wt % PTFE matrix obtained in the tests carried out with P 240 abrasive with the grain size of 58.5 μm. It follows from the data presented in Fig. 6 that the abrasive wear resistance of the hybrid matrix containing the nanosized fillers is close to that of the matrix itself (bars *2*, *6*, and *7*), while the abrasive wear resistance of the composites filled with the microsized particles exceeds that of the matrix (bars *3* and *4*). A similar pattern of abrasive wear is also observed for the composites with the hybrid matrix that contains the coarse fluoroplastic particles.

The filler size has a similar effect on the roughness of the friction surfaces R_a (Fig. 6), which is illustrated by the microphotos of the worn surfaces of the original UHMWPE + 10 wt % PTFE matrix (Fig. 7a), as well as of the nano- and microcomposites based on this matrix (Figs. 7b–7d). The comparable cutting traces on the surfaces of the matrix and the nanocomposites (Fig. 8) show that fairly soft PTFE is incapable of protecting the matrix from the effect of fixed abrasive. In the microcomposites, the particle size of the filler is comparable with the grain size of abrasive, and these particles can protect the matrix against wear; the coarser the particles of the microsized filler, the greater their contribution to the abrasive wear resistance of the composites [11]. During abrasive wear, PTFE only facilitates the sliding of the counterface covered with abrasive cloth over the surface of the composite specimen.

DISCUSSION

A complex analysis of the tribological characteristics of the nano- and microcomposites with the hybrid UHMWPE + 10 wt % PTFE matrix carried out for three modes of wear has shown that, during dry sliding friction, fine PTFE forms a uniform transfer film on the counterface (the polymer–polymer friction pair), which ensures the high wear resistance of both the nano- and the microcomposites [10]. In this case, the supramolecular structure produced in the nano- and microcomposites with the hybrid matrix does not make a significant contribution to their wear resistance. The temperature of the friction surfaces of the nano- and microcomposites does not also substantially change as compared with that on the friction surface of the original matrix and, therefore, does not

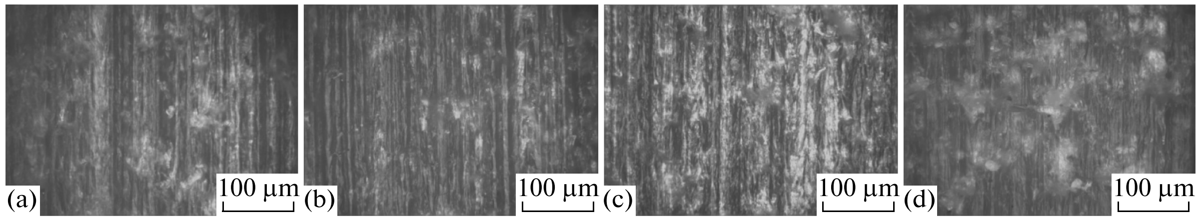

Fig. 7. Microphotos of worn surfaces of (a) UHMWPE + 10 wt % PTFE matrix; (b) UHMWPE + 10 wt % PTFE + 0.5 wt % SiO_2; (c) UHMWPE + 10 wt % PTFE + 0.5 wt % UNV; (d) UHMWPE + 10 wt % PTFE + 20 wt % Al_2O_3 after friction over R240 abrasive cloth.

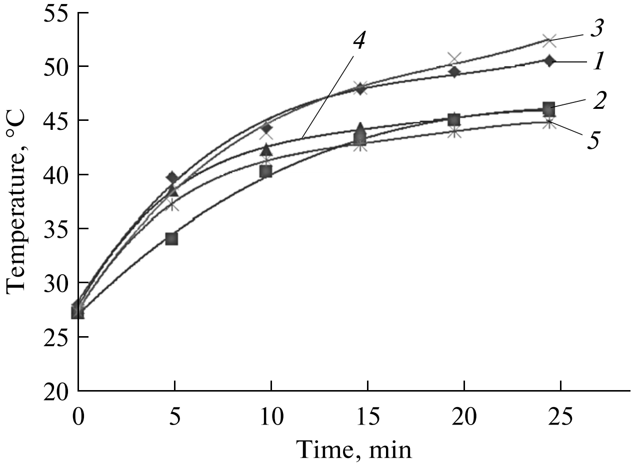

Fig. 8. Kinetic curves of temperature of surfaces of (*1*) unfilled UHMWPE; (*2*) UHMWPE + 10 wt % PTFE; (*3*) UHMWPE + 10 wt % PTFE + 20 wt % AlO(OH); (*4*) UHMWPE + 10 wt % PTFE + 0.5 wt % UNV; and (*5*) UHMWPE + 10 wt % PTFE + 0.5 wt % AlO(OH).

play a noticeable role in the wear process (Fig. 8). The factor that determines the wear resistance of the composites is the fluoroplastic transfer film on the counterface. This is confirmed by the increasing role of the nanosized fillers as the solid lubricant in the composites with the hybrid matrix containing the coarse fluoroplastic particles. The particle size of the fluoroplastic determines the uniformity of its distribution in the matrix and, therefore, the quality of the transfer film on the counterface, i.e., the constancy of its thickness. A comparative analysis of the tribological characteristics of the nano- and microcomposites with the UHMWPE matrix and the hybrid UHMWPE + 10 wt % PTFE matrix (containing fine fluoroplastic) has shown that the effect of the nanosized fillers as a solid lubricant is equivalent to the effect of the fluoroplastic transfer film under conditions of dry sliding friction [8, 10]. For example, the wear resistance of UHMWPE filled with the nanosized particles and fine fluoroplastic increases by four to six times.

Under the conditions of abrasive wear, the cutting of the matrix and soft PTFE by particles of fixed abrasive occurs; therefore, the abrasive wear resistance of the composites is governed by the grain size of abrasive and the strength of the supramolecular structure formed, as this takes place for the UHMWPE–PTFE matrix. Polytetrafluoroethylene only facilitates the sliding of the abrasive cloth over the surface of the polymer specimen.

Since the introduction of the nano- and microsized fillers into the hybrid UHMWPE–PTFE matrix containing fine (14 μm) fluoroplastic particles increases the wear resistance of the matrix only slightly, the nanosized fillers and fluoroplastic can be exchangeable when wear-resistant solid lubricating UHMWPE-based composites are developed for various operating conditions of articles, such as heavy loads, low temperatures, and corrosive media.

CONCLUSIONS

The role of PTFE as the solid lubricant under the conditions of dry sliding friction and boundary lubrication is equally significant both for the hybrid UHMWPE + 10 wt % PTFE matrix and for the composites based on this matrix.

During the abrasive wear of the composites with the hybrid matrix, fairly soft PTFE only facilitates the sliding of the abrasive cloth over the surface of the polymer specimen, and the abrasive wear resistance of the composites is determined by the ratio of the grain size of abrasive to the particle size of the filler, as well as by the strength of supramolecular structure.

The efficiency of using the hybrid UHMWPE + 10 wt % PTFE matrix to develop extrudable solid-lubricating wear-resistant composites with a high molecular weight matrix is governed by the operating conditions of these composites, such as medical applications like endoprostheses, heavy loads, and corrosive media.

ACKNOWLEDGMENTS

This work was carried out using the equipment from the Nanotekh Center of Collaborative Access of the Institute of Strength Physics and Materials Science of the Siberian Branch of the Russian Academy of Sciences and from the analytical center of the Tomsk Polytechnic University and was supported by the Russian Foundation for Basic Research and the Belarusian Republican Foundation for Basic Research (projects nos. 12-08-00930_a, 13-08-98068, and 14-08-90028 (T14R-210)).

NOTATION

I	wear rate, mm^2/min
σ_u	ultimate strength, MPa
ε	relative elongation, %
R_a	roughness of friction surface, μm

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Translated by D. Tkachuk