

Solid-Lubricant, Polymer – Polymeric and Functionalized Fiber– and Powder Reinforced Composites of Ultra-High Molecular Weight Polyethylene

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Abstract. Mechanical and tribotechnical characteristics of solid-lubricant and polymer-polymeric composites of UHMWPE were studied for the sake of design extrudable, wear-resistant, self-lubricant polymer mixtures for Additive Manufacturing (AM). Tribotechnical properties of UHMWPE blends with the optimized content of solid lubricant fillers (polytetrafluoroethylene, calcium stearate, molybdenum disulphide, colloidal graphite, boron nitride) were studied under dry sliding friction at different velocities ($V = 0.3$ and 0.5 m/s) and loads ($P = 60$ and 140 N). Also, in order to increase strength and wear-resistance of UHMWPE composites they were reinforced with wollastonite microfibers and aluminum metahydroxide AlO (OH) microparticles preliminary treated (functionalized) in polyorganosiloxane. The comparison on measured mechanical and tribotechnical properties are given with interpretation of the mechanisms of observed phenomenon.

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) possesses high enough strength properties as well as the low friction coefficient, high wear- and chemical resistance in aggressive environment. For this reason, it is applied for manufacturing friction units of machine parts and mechanisms. Also, it has found wide application in medicine for fabricating components of orthopedic implants (artificial joints) [1–3]. Extrudable high-strength and solid lubricant nano- and microcomposites based on ultra-high molecular weight (UHMWPE) matrix are intensively developed recently [1–6]. However, due to the chemical inertness of the UHMWPE–matrix, at loading of various additives (mostly, mineral fillers) no chemical bonds are formed at the interphase boundaries. This is manifested in extremely low interphase adhesion. In this context, it is of importance to study addition of micron size fillers into UHMWPE with functionalization of the former using coupling agents (compatibilizers/adhesion promoters) in order to improve the mechanical and tribotechnical characteristics of composites.

Besides the adhesion problem, because of the long polymer chains (molecular weight of 4.0×10^6 c.u.), UHMWPE possesses extremely low melt flow index (MFI– 0.06 g/10 min) that limits its processing by traditional methods for structural plastics such as injection moulding, screw extrusion, etc. In so doing, the issues of improving the processability (extrudability) of composites based on the high molecular weight matrix, in particular UHMWPE, are remained unresolved.

In order to develop extrudable powder composites for further application in additive manufacturing (AM) at fabricating the complex shape components of the friction units for mechanical engineering and medicine, the flowability and tribomechanical characteristics of polymer-polymeric mixtures of UHMWPE with the block–copolymers of linear low-density polyethylene with polypropylene (PP-b-LLDPE) as well as the cross-linked polyethylene (PEX-b) were studied. The ultimate aim was the further development the composites with a multiply increased wear resistance and satisfactory melt flowability (MFI) [7–11]. The use of extrudable composites in AM technologies allows one to design high-strength and wear-resistant products of complex shape, including friction units for the machines operating under the harsh environment and loading conditions [7–12].



2. Results and Discussion

UHMWPE powder (GUR-2122, Ticona) with a molecular weight of 4.0×10^6 c.u., cross-linked polyethylene PEX-b, block copolymers of PE with polypropylene (PP-b-LLDPE) particle size ~ 100 – 200 μm , grafted high density polyethylene HDPE-g-VTMS (particle size 100 – 300 μm), were used for the specimen preparation; as well as solid lubricant powders of: (i) polytetrafluoroethylene (PTFE, $\varnothing 14$ μm), (ii) molybdenum disulphide (MoS_2 , $\varnothing 1$ – 7 μm), (iii) colloidal graphite (CG $\varnothing 1$ – 4 μm), (iv) calcium stearate (CS, $\varnothing 1$ – 7 μm) and (v) hexagonal boron nitride (NB, $\varnothing 10$ μm).

Wollastonite microfibers ($\varnothing 10$ μm , aspect ratio 5 : 1) (GEOKOM CJSC, Kaluga region), and micropowder of aluminum metahydroxide $\text{AlO}(\text{OH})$ ($\varnothing 2$ – 5 μm) (modifying additive TS-104, Techno-Service Ltd., St. Petersburg) were used for specimen preparation. To modify the filler surfaces, the Penta-1006 liquid reagent (, PENTA-91 ltd. Russia) was used. The latter represents a composite based on poly-[oxy(dimethylsilylene), $[\text{R}_2\text{SiO}]_n$ where R is the oxygen-containing high-molecular-weight organosilicon compounds] [13].

Functionalization of fillers was carried out by their treatment in water-ethanol (pH 4.5-5.5) solutions with added Penta-1006 modifier at ambient temperature with continuous mixing for 5 min. The content of the Penta-1006 reagent was 1 wt % related the filler weight (or 0.2 wt % over the total weight of the powder mixture). The suspension was then dried in oven at the temperature of $T = 120^\circ\text{C}$.

The bulk specimens of polymer composites were fabricated by compression moulding at the specific pressure of 10 MPa and the sintering temperature $T = 200^\circ\text{C}$ with subsequent cooling rate of 3 – 4 $^\circ\text{C}/\text{min}$. Powders of UHMWPE and fillers (PP-b-LLDPE, PEX-b and nanoparticles) were mixed in a planetary ball mill MP/0.5*4 with preliminary dispersion of the components in an ultrasonic bath in alcohol suspension.

The wear resistance of the specimens under the dry sliding friction was determined by a “block-on-ring” scheme with the 2070 SMT-1 friction testing machine (following the ASTM G99 and DIN 50324). The loading applied to a specimen fixed in a holder was $P = 60$ and 140 N while the sliding velocities were equal to $V = 0.3$ and 0.5 m/s. The size of the specimens was $15.8 \times 6.4 \times 10.0$ mm^3 . The diameter of the counterbody made of the bearing steel (HRC 60) steel was 35 mm.

The roughness of the wear track surface as well its volume (being proportional to wear factor) of the specimens was examined by the Step IQ (KLA-Tencor) profilometer.

The degree of crystallinity was determined with the use of SDT Q600 combined analyzer. IR-spectra were recorded with the help of NIKOLET 5700 (Thermo Fisher Scientific, USA) spectrometer. The structural studies were carried out with the use of LEO EVO 50 (Carl Zeiss, Germany) scanning electron microscope at the accelerating voltage of 20 kV. So, the rupture surface were prepared by mechanical bending fracture of the notched specimens after the preliminarily exposure in liquid nitrogen.

Table 1 show the data on mechanical properties of the polymer-polymeric mixtures of UHMWPE with the fillers with the optimized content [7–10] in terms of the extrudability degree (proportional to the MFI) and the minimum decrease in the mechanical characteristics of the mixtures (yield point $\sigma_{0.2}$, ultimate strength σ_U , value of elongation at break ϵ). The revealed dependencies of the mechanical and tribotechnical properties of polymer mixtures versus the filler weight fraction carried out in [7–11] have shown that for all the fillers under study (Table 1), the optimum filler loading makes 5–10 wt %. For this reason, the composites with the optimum compound of the polymer mixture were chosen to study the effect of the sliding velocity and load on the wear resistance.

The physical and mechanical properties of UHMWPE composites loaded with 20 wt % of the wollastonite and 20 wt % aluminum metahydroxide are given in Table 2. It follows from the table that the density and hardness of UHMWPE composites increase with enlarging weight fraction of the microfibers and microparticles. We suggest that initiation of the hydrolysis process would not affect values of these parameters.

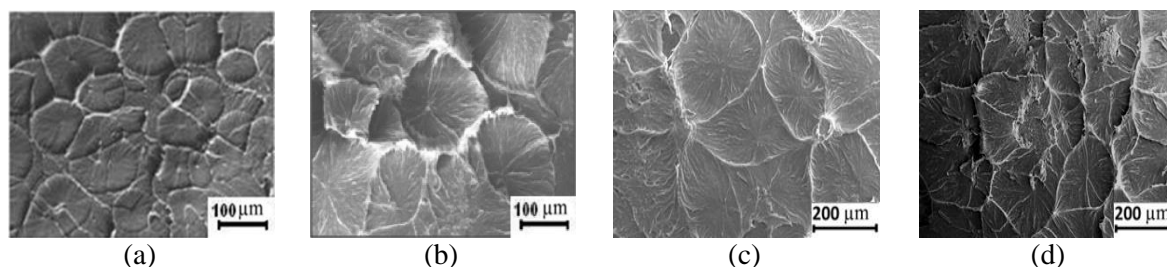
Table 1. Physical-Mechanical and tribotechnical properties of UHMWPE and its composites

Filler content, wt %	Density, g/cm ³	Shore hardness <i>D</i>	Elastic modulus <i>E</i> , MPa	Yield point $\sigma_{0.2}$, MPa	Ultimate strength σ_U , MPa	Elong. at break ϵ , %	Extrud. temp./pressure, °C/MPa	MFI, g/10 min
UHMWPE	0.928	55.6±0.2	405±17	22.1±0.4	36±1.6	482±6	205/5.52	0.126
UHMWPE + 10% HDPE-g-VTMS	0.924	57.6±0.5	398±9	22.5±0.9	29.0±1.3	416±57	205/5.52	0.291
UHMWPE + 10% PEX-b	0.931	57.4±0.5	354±39	22.8±0.8	31.2±2.9	429±38	205/4.69	1.122
UHMWPE + 5% PP-b-LLDPE	0.916	56.1±0.5	403±25	21.1±0.5	29.4±1.6	383±28	205/4.34	3.574

Table 2. Physical-mechanical properties of UHMWPE and its composites

Filler content, wt %	Density, g/cm ³	Shore hardness <i>D</i>	Elastic modulus <i>E</i> , MPa	Yield point $\sigma_{0.2}$, MPa	Ultimate strength σ_U , MPa	Elong. at break ϵ , %
UHMWPE + 20 wt % Wollast	1.062	58.9 ± 0,7	501 ± 30	24.7 ± 1.1	36.8 ± 5.7	454 ± 60
UHMWPE+ 20 wt % AIO(OH)	1.07	60.23 ± 0.6	509 ± 55	21.9 ± 1.3	33.2 ± 1.9	425 ± 39
UHMWPE + 20 wt % Wollast. + 0.2% Penta 1006 (hydrolysis)	1.062	59.19 ± 0.6	620 ± 46	25.2 ± 1.3	34 ± 4	415 ± 23
UHMWPE + 20 wt % AIO(OH) + 0.2% Penta 1006 (hydrolysis)	1.064	59.4 ± 0.5	564 ± 19	23.1 ± 0.5	37.0 ± 1.5	446 ± 26

The permolecular structure typical for UHMWPE (a) and all polymer mixtures under study at the filler content up to 10 wt % (b–d) are given in Fig. 1. It is shown that with the further increase of the filling degree, a spherulitic structure is not formed, and the degree of crystallinity of the polymer-polymeric composites is substantially reduced [7, 8]. At the same time, the mechanical properties are also substantially decreased (yield strength, ultimate strength, value of elongation at break). For this reason, the criterion for choosing polymer processing modifier for UHMWPE should be the balance between satisfactory flowability of the mixture and lowest loose of strength characteristics.

**Figure 1.** SEM micrographs of permolecular structure of UHMWPE (a) and its composites “UHMWPE + 10 wt % HDPE-g-VTMS” (b), “UHMWPE + 10 wt % PEX-b” (c), “UHMWPE + 5 wt % PP-b-LLDPE” (d)

Polypropylene has the higher melt flowability (MFI = 0.6 g/10 min). However it does not possess thermodynamic affinity to UHMWPE and its loading substantially reduces the strength properties of the mixture due to lack of adhesion (Table 1). A block copolymer of the polypropylene with the linear low density polyethylene (PP-b-LLDPE) provides better adhesion to UHMWPE and maximizes the strength characteristics of the matrix (Table 1). The analysis of the IR-spectra of UHMWPE blends with the block copolymer PP-b-LLDPE showed the increased peak intensity at 1240 cm^{-1} (C-O-C), 1040 cm^{-1} (C-C-O), 1620 cm^{-1} (C = C) and 1700 cm^{-1} (C = O) for the spectra of polymer-polymeric composites which testifies for the bonding between UHMWPE and the block copolymer [8]. In other words, by adding a block copolymer containing the linear low-density polyethylene it was possible to mechanically and chemically “bond” the fillers containing polypropylene with the UHMWPE matrix. As a result, the flowability (extrudability) increased while the minimum loss of mechanical properties took place (under the conditions of the adhesion of UHMWPE with processing filler).

Analysis of the permolecular structure of powder and fiber filled UHMWPE composites shows that at loading of 20 wt % of the fillers the spherulitic structure is no longer formed. Microfibers and microparticles are evenly distributed in the matrix. The degree of crystallinity in the composites does not exceed 15 % [7, 8].

Physical and mechanical properties of polymer-polymeric mixtures of UHMWPE with solid-lubricant fillers of optimum content were determined by the authors earlier [7]. It was motivated by reaching maximum level of wear resistance and retaining the spherulitic permolecular structure of the composite (see Table 3). As follows from the table the Shore D hardness of UHMWPE composites is determined solely by the type of filler: the composite with calcium stearate possesses the lowest hardness (54.3), while the composite with molybdenum disulfide MoS₂ has the highest one (57.4). The value of ultimate strength σ_U for all composites has decreased as compared with the neat polymeric matrix. The value of elongation at break ε of the composites also decreases or increases with respect to UHMWPE depending on the type of the filler varying in the range 360–503 %. In other words, all the fillers for the ultra-high-molecular weight matrix (UHMWPE) under investigation cannot be treated as the reinforcing ones.

The degree of crystallinity of the UHMWPE composites with increasing weight fraction of all the above mentioned solid lubricant particles is decreased (Table 3). However, the type of the permolecular structure remains spherulitic (Fig. 2). It was found that various solid-lubricant fillers provided different wear resistance of the UHMWPE composites, which also depends on sliding velocity and applied load. The values of the friction coefficients for all the studied composites are presented in Table 3. It is easily seen that for most of them the friction coefficient has decreased by 60–70 %. Further studies of the UHMWPE based mixtures were focused on their wear resistance at various sliding velocities ($V = 0.3$ and 0.5 m/s) and loads ($P = 60$ and 140 N).

Table 3. Physical-mechanical properties of UHMWPE and its composites

Composition	Density ρ , g/cm ³	Shore hardness D	Ultimate strength σ_U , MPa	Elongation at break ε , %	Crystallinity χ , %	Friction coefficient f
UHMWPE	0.928	55.6 ± 0.2	36 ± 1.6	482 ± 6	56.5	0.12
UHMWPE + 5 wt % PTFE	0.951	54.5 ± 0.6	29.2 ± 1.0	465 ± 23.6	39.5	0.07
UHMWPE + 5 wt % CS	0.913	54.3 ± 0.2	33.1 ± 0.9	411 ± 19.5	41.0	0.11
UHMWPE + 5 wt % MoS ₂	0.928	57.4 ± 0.3	28.9 ± 1.6	500 ± 25.3	43.6	0.8
UHMWPE + 5 wt % CG	0.953	56.8 ± 0.3	29.7 ± 1.5	503 ± 25.1	42.1	0.08
UHMWPE + 5 wt % BN	0.955	55.7 ± 0.4	24.1 ± 0.9	360 ± 16.4	41.2	0.08

Loading of the functionalized wollastonite also demonstrates high efficiency at high sliding velocity of $V = 0.5$ m/s (Fig. 3b). At the high applied loads the wear multiplies by the factor of 5–10 at both sliding velocities for pure UHMWPE and its composites with functionalized fillers (Fig. 3). In doing so, the composites containing the wollastonite treated by polyorganosiloxane with the initiated hydrolysis process at the high load provides the highest wear resistance among all the studied blends. This testifies for the efficiency of this technique of the filler treatment in comparison with a simple mechanical mixing of the composite components.

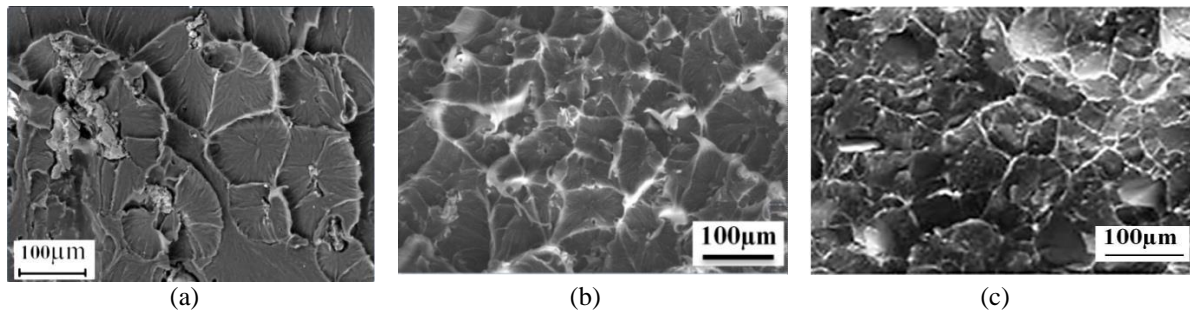


Figure 2. Permolecular structure of composites based UHMWPE with 5 wt % PTFE(a), 5 wt % MoS2 (b), 5 wt % CG (c)

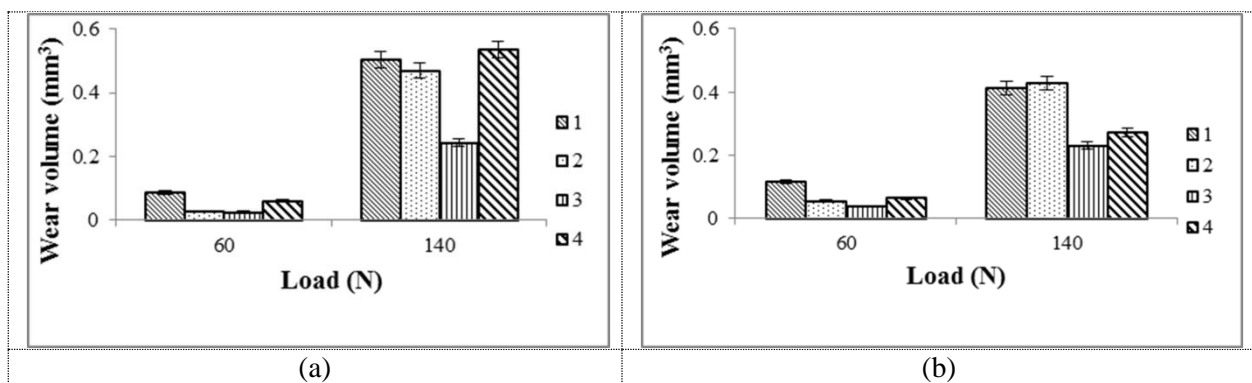


Figure 3. Volumetric wear (mm^3) at sliding velocities $V = 0.3$ (a) and 0.5 m/s (b) of UHMWPE (1) and its composites with 20 wt % of wollastonite (2), UHMWPE + 20 wt % of wollastonite + 0.2 wt % Penta 1006 with hydrolysis (3) and UHMWPE + 20 wt % of wollastonite + 0.2 wt % Penta 1006 without hydrolysis (4) at the loads $P = 60$ and 140 N

When UHMWPE is filled with the functionalized aluminum metahydroxide particles with initiating the hydrolysis, wear decreases both at moderate and high sliding velocities ($V = 0.3$ and 0.5 m/s) at the load of $P = 60$ N (Fig. 4). With increasing the load up to $P = 140$ N the wear of UHMWPE and its composites also multiply increases at both sliding velocities.

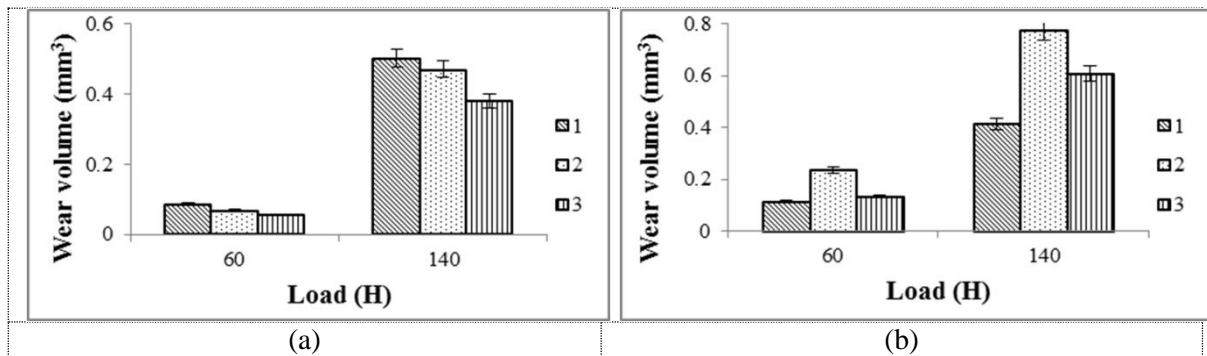


Figure 4. Volumetric wear (mm^3) at the sliding velocities $V = 0.3$ (a) and 0.5 m/s (b) of the UHMWPE (1) and its composites UHMWPE + 20 wt % AlO (OH) (2), UHMWPE + 20 wt % AlO (OH) + 0.2 wt % Penta 1006 with hydrolysis (3) at loads $P=60$ and 140 N

The volumetric wear diagram for all the composites studied is shown in Fig. 5, at the moderate sliding velocity ($V = 0.3$ m/s) and loads of $P = 60$ and 140 N. It is seen from the diagram that at low load $P = 60$ N the wear resistance of the composites increases by 2–3.5 times. The temperature at the counterface surface makes $T = 27\text{--}30^\circ\text{C}$. Note, that the most efficient solid lubricant filler for the UHMWPE under these testing conditions is polytetrafluoroethylene.

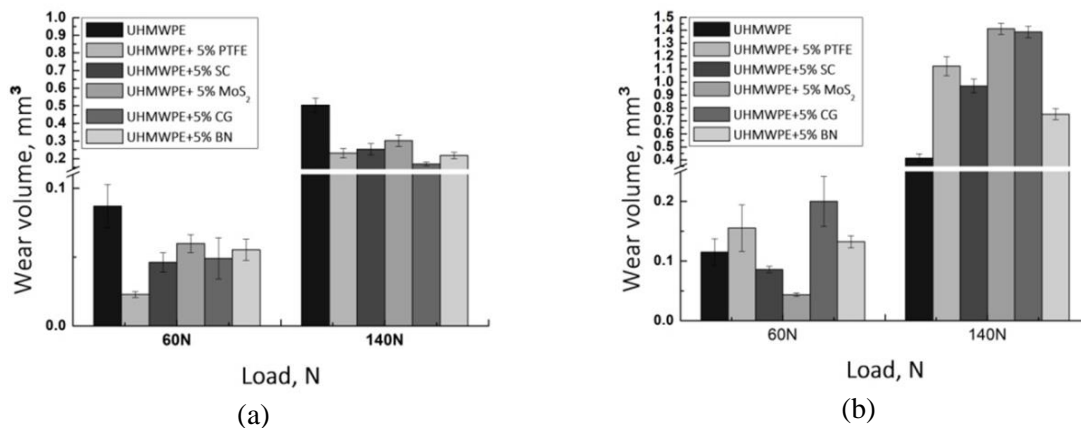


Figure 5. Volumetric wear of UHMWPE and its composites at the steady-state wearing stage. Sliding velocity 0.3 (a) and 0.5 m/s (b), and loads 60 and 140 N

At the load of $P = 140$ N the wear resistance of the UHMWPE and its composites decreases more than twice. In doing so, the temperature at the counterface surface (that should be equal to one at wear track specimen surface) increases from 27 to 39°C .

At higher sliding speed ($V = 0.5$ m/s) and moderate load ($P = 60$ N) the wear of the neat UHMWPE as well as its composites is twice higher than that at the sliding velocity of $V = 0.3$ m/s (Fig. 5b). At these loading conditions the molybdenum disulphide provides the most efficient wear resistance. This means that it can be used as solid lubricant filler for fabricating the products, which operate in friction units at moderate loads and high sliding velocities.

Finally, at high sliding velocity and load (up to $P = 140$ N) a multiple increase in the wear of the UHMWPE and all its composites takes place (by the factor of 5–10). In doing so, the temperature of the friction surface rises up to $T = 64^\circ\text{C}$.

3. Conclusions

The physical-mechanical and tribotechnical properties of the polymer-polymeric, solid lubricant and functionalized fiber and powder reinforced composites based on UHMWPE at different sliding velocities ($V = 0.3$ and 0.5 m/s) and loads ($P = 60$ and 140 N) under dry sliding friction have been studied. It is shown that the treatment of the fibrous and powder fillers by the polyorganosiloxane with initiating the hydrolysis process increases the mechanical characteristics of composites based on the high molecular weight PE matrix by 10 %. The wear resistance of the microcomposites increases twofold at sliding velocities $V = 0.3$ m/s and 0.5 m/s at the moderate load ($P = 60$ N) as compared to the neat UHMWPE. When the load is increased up to $P = 140$ N, the wear resistance of the composites is sharply reduced. For this reason, micro-composites UHMWPE based with the functionalized fibrous and powder fillers can be recommended for operation in friction units operating in a wide range of sliding velocities (up to $V = 0.5$ m/s) and at the moderate loads up to $P = 60$ N. The technique for compatibilizing mineral fillers (fibrous and powder) with the high molecular weight PE matrix by the treatment in the polyorganosiloxane can be applied as an efficient approach for increasing the wear resistance of highly filled UHMWPE composites.

The wear resistance of solid lubricant UHMWPE composites at the moderate sliding velocity ($V = 0.3$ m/s) and load ($P = 60$ N) increases by 2–3 times in comparison with pure UHMWPE. However, when increasing the load up to $P = 140$ N the wear resistance of UHMWPE and its composites is reduced twice. At high sliding velocity and load (up to $P = 140$ N) the multiple increase in wear of the UHMWPE and all its composites (by the factor of 5–10) occurs.

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