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THE EFFECT OF PHYSICAL-CHEMICAL NATURE OF UHMWPE AND PPS THERMOPLASTIC MATRICES ON THE FORMATION OF MECHANICAL AND TRIBOLOGICAL PROPERTIES OF THEIR CARBON FIBER FILLED COMPOSITES

S. V. Panin,[1,2] L. A. Kornienko,[1] Le Thi My Hiep,[2]
V. O. Aleksenko,[1] and D. G. Buslovich[1,2]

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The effect of carbon fiber dimensions on mechanical and tribological properties of the composites based on two thermoplastic matrices of different physical-chemical nature (polyphenylene sulfide, PPS, and ultrahigh molecular weight polyethylene, UHMWPE) is compared. It is shown that the supermolecular structure formed by compression sintering of PPS and UHMWPE controls the distribution pattern of carbon fibers in the matrix, which affects the level of tribological properties. The composites on a high-strength PPS-matrix, designed for structural/tribotechnical applications and loaded with short carbon fibers (70 μm), can be fabricated at a high loading degree (40 wt.%), which provides a five-fold increase in wear resistance and a 1.7-fold decrease in friction coefficient. The wear resistance increases due to the formation of a third body consisting of wear debris, which essentially reduces the friction coefficient. Loading the PPS with carbon nanofibers modifies the polymer matrix structure through the dispersion hardening mechanism but does not improve its tribological properties. Adding chopped carbon fibers (with a length of a few millimeters) into the PPS matrix gives rise to substantial hardening but significantly degrades the tribological properties. The UHMWPE composites can be manufactured via filling the matrix with 10 wt.% chopped carbon fibers evenly distributed in it. Carbon nanofibers are thought to be the most efficient fillers for the UHMWPE matrix of a spherulitic supermolecular structure in terms of increasing its wear resistance. They play the role of a solid lubricant medium (wear resistance increases 2.7 times, the friction coefficient is decreased twice). Comparatively long chopped carbon fibers of the millimeter range (2–3 mm) play a reinforcing role in contrast to the short carbon fibers measuring tens and hundreds of micrometers (70, 200 μm). They neither increase the friction coefficient nor result in the abrasive wear of the steel counterpart. The role of interphase adhesion, polymer matrix hardness, its chemical reactivity and supermolecular structure in forming the tribomechanical properties of carbon composites based on thermoplastic matrices of different physical-chemical nature is discussed.

Keywords: ultra-high molecular weight polyethylene, polyphenylene sulfide, carbon fibers, wear resistance, supermolecular structure.

INTRODUCTION

Antifriction polymer composites are widely used in tribotechnical systems, in state-of-the-art technological structures as sealing elements, and in medical systems, ensuring their reliability and durability. Antifriction polymer-

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[1] Institute of Strength Physics and Materials Science of the Siberian Branch of the Russian Academy of Sciences, Tomsk, Russia, e-mail: svp@ispms.tsc.ru; rosmc@ispms.tsc.ru; vl.aleksenko@mail.ru; [2] National Research Tomsk Polytechnic University, Tomsk, Russia, e-mail: myhiepru@gmail.com; dgb2@tpu.ru. Translated from Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika, No. 4, pp. 22–29, April, 2020. Original article submitted October 12, 2019; revision submitted March 10, 2020.

based composite materials can be designed in different ways, in particular: by reinforcing or hardening a self-lubricating polymer matrix (PTFE, polyamide, UHMW, etc.) with (nano)particles/fibers aimed at improving its mechanical properties and ensuring a low friction coefficient at a level of non-filled polymer; b) by introducing solid-lubricant particles (PTFE, MoS_2, graphite, etc.) into a high-strength polymer matrix (PEEK, PPS, PI, etc.), ensuring a formation of a high-wear-resistance transfer film on the counterpart, which preserves strain-hardened properties of a non-filled polymer. In the latter case, common practices involve the use of both reinforcing fibers and solid-lubricant particles. According to these approaches, the response of the polymer composites to an application of friction loading is different, so a study of the behavior of their deformation and wear would allow formulating recommendations on improving the resistance to application of contact loading, specifically, in the case of sliding friction.

UHMWPE, having long molecular chains, is characterized by high reversible deformation (due to semicrystalline structure), capability of damping elastic vibrations (due to fibrillous structure), and stability to tribo-oxidation and scuffing under the low load-velocity tribological conditions [1–6].

While PPS is a promising high-temperature structural thermoplastic polymer material [7–11], when unfilled (being a structural material but without antifriction properties), it possesses low wear resistance and high friction coefficient (>0.34) In contrast to UHMWPE, PPS due to its high hardness (Shore D hardness value of about 80) possesses a low dampening capacity. The processes of tribooxidation and scuffing develop in it very fast, and the impact of the tribo-oxidized wear products dramatically intensifies microabrasive wear, including the counterpart wear.

In addition to antifriction applications, thermoplastic polymers due to the ease of their recycling are extensively used for fabrication of polymer composites for structural applications. One of the most common approaches is loading of carbon fibers of different dimensions [12–16]. The decisive factor for improving mechanical properties is adhesion between the composite components. From this standpoint, PPS as a more active component can ensure a multiple increase in the strength properties, while reinforcement of nonpolar UHMWPE does not allow increasing, e.g., the elastic modulus, by more than a factor of 1.4 – 2.0 without a special treatment of the fibers.

Considering the aforementioned, in this study we aim at performing a comparative analysis of mechanical and tribological properties of polymer composites based on a soft UHMWPE matrix and a high-strength PPS matrix with carbon fibers of different lengths (in the nano-, micro-, and millimeter ranges). By selecting the matrices and the content of fillers, one can intentionally change the functional properties and extend the range of applications and the line of products for mechanical engineering, engineering chemistry, agriculture, and other areas of technology. In this study we discuss the role of the physical-chemical nature of thermoplastic matrices in forming the structure and the role of the latter in ensuring the mechanical and tribological properties of composite materials.

EXPERIMENTAL MATERIALS AND PROCEDURES

In the experiments we used a PPS powder manufactured by Ticona, Germany (Fortron grade 0205B4) with an average particle size of 20 μm and a UHMWPE powder (GUR-2122) manufactured by Ticona, Germany with a molecular mass of 4.5 million amu and a particle size within 5–15 μm, carbon nanofibers (CNFs) of the Taunit grade produced by NanoTechCenter, LLC, Tambov, Russia (Ø 60 nm, length 2–3 μm), milled carbon fibers (MCFs) of the average lengths $l \approx 70$ and 200 μm (Ø 7.5 μm) and chopped carbon fibers (CCFs) of an average length of $l \approx 2$ mm. The experimental composites were fabricated by compression sintering. The CNF filler content was chosen to be 0.3 wt.% (for PPS) and 0.5 wt.% (for UHMWPE) to rule out agglomeration. The content of MCFs and CCFs for PPS (having a high melt flow index) was chosen to be 40 wt.%, primarily to improve the strength properties. For the high-viscosity UHMWPE the MCF and CCF filler content was reduced to 10 wt.% in order to ensure structure homogeneity.

Shore D hardness was measured in an Instron 902 universal testing machine in accordance with ASTM D 2240. Three-point bending tests of PPS composites were performed in an Instron 5582 electromechanical testing machine. Mechanical properties of UHMWPE composites were determined in tensile tests in an Instron 5582 electromechanical testing machine by tensile loading of dumb-bell shaped samples (GOST 11262-80).

Pin-on-disk volumetric wear testing of the samples in the dry sliding friction mode was performed in a CSEM CH2000 tribometer (CSEM, Switzerland) at a load of 5 N (contact pressure $[P_{\max}] = 31.8$ MPa) and a sliding velocity of 0.3 m/s. The counterpart (GCr15 steel ball) radius was 6 mm. To examine the wear track surface roughness of the

TABLE 1. Physical-Mechanical Properties of PPS and PPS-Composites with Carbon Fibers

Filler content, wt.%	Density ρ, g/cm^3	Shore D hardness	Elastic modulus *E*, GPa	Ultimate tensile strength σ_{UTS}, MPa	Elongation at break ε, %	Crystallinity degree χ, %
PPPS	1.33	79.5 ± 0.5	3.9 ± 0.07	97.8 ± 1.6	2.56 ± 1.4	50.6
0.3% CNF	1.35	78.7 ± 0.2	3.8 ± 0.3	78.4 ± 8.2	1.95 ± 1.5	55.2
40% MCF (70 μm)	1.48	83.2 ± 0.3	9.9 ± 0.9	104.5 ± 8.7	1.05 ± 0.5	25
40% MCF (200 μm)	1.47	84.1 ± 0.4	13.5 ± 0.8	147.8 ± 4.3	0.99 ± 0.1	-
40% CCF (2 mm)	1.43	83.3 ± 0.9	13.8 ± 1.7	164 ± 23	1.3 ± 0.2	27.7

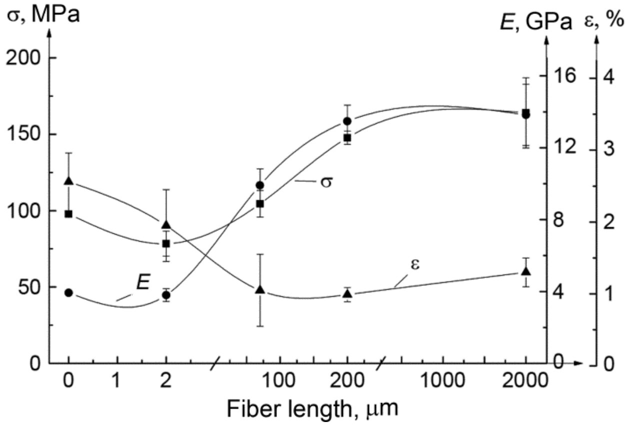

Fig. 1

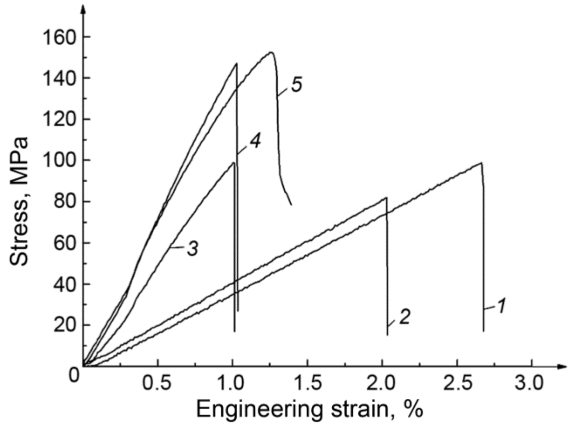

Fig. 2

Fig. 1. Mechanical properties of PPS and PPS-composites as a function of the carbon fiber length.

Fig. 2. Engineering stress-strain curves for PPS (Curve *1*) and its composites loaded with 0.3 wt.% CNFs (Curve *2*); 40 wt.% MCFs (70 μm) (Curve *3*); 40 wt.% MCFs (200 μm) (Curve *4*); 40 wt.% CCFs (2 mm) (Curve *5*).

samples a New View 6200 optical profilometer (Zygo) was used. Supermolecular structure of the composites was observed in a LEO EVO 50 (Carl Zeiss) scanning electron microscope at an accelerating voltage of 20 kV on the rupture surfaces of notched sample mechanically fractured following their exposure in liquid nitrogen.

RESULTS AND DISCUSSION

Table 1 lists the physical-chemical properties of PPS-composites with carbon fibers (CFs) of different dimensions (nano-, micro-, and millimeter lengths). It is seen that the mechanical properties of nanocomposites (hardness, elastic modulus, ultimate tensile strength, elongation at break) change by about 10–13% compared to the unfilled polymers. In the composites filled with MCFs and CCFs, the elastic modulus and the ultimate tensile strength increase by 2.5–3.5 and 1.1–1.7 factors, respectively, while the elongation at break decreases by a factor of 1.9–2.5. Figures 1 and 2 present the mechanical characteristics of PPS composites varying with the carbon fiber size.

Here we studied the supermolecular structure of PPS and its composites, with Fig. 3 presenting SEM images of the supermolecular structure. It is seen that a dense fragmented structure is formed in the filled PPS composites. The filler particles are assumed to be concentrated mostly along the initial powder particle boundaries, which was set by the

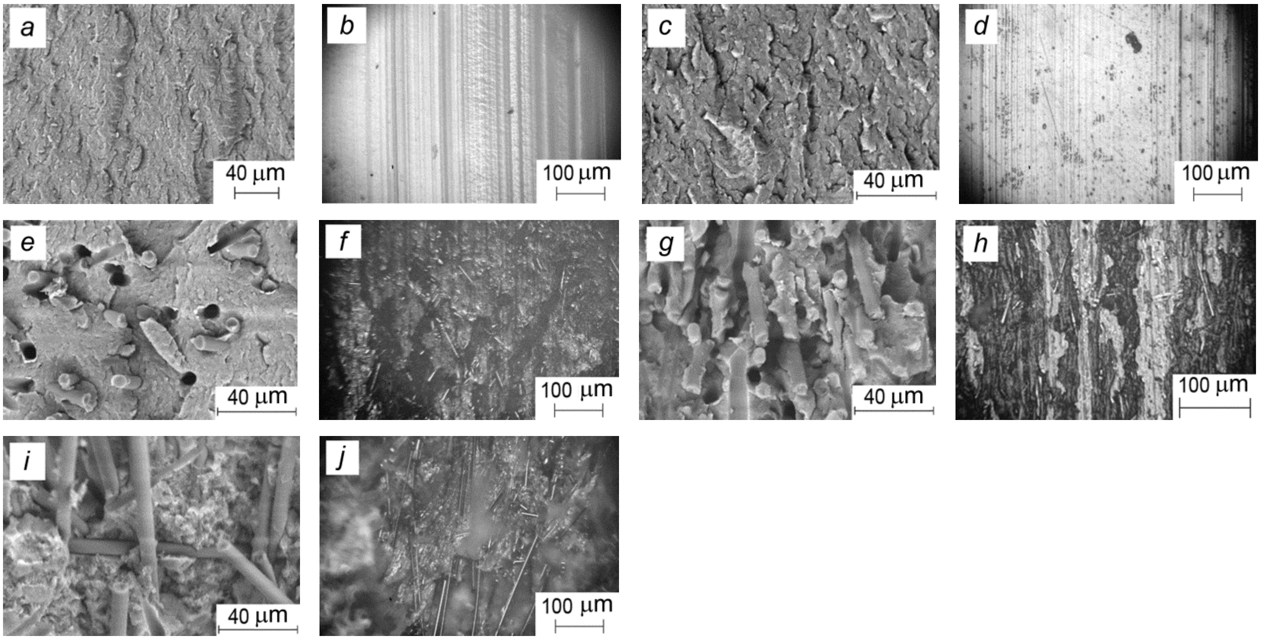

Fig. 3. SEM-micrographs of the supermolecular structure and optical images of the wear surfaces of PPS (*a*, *b*) and PPS –composites filled with 0.3 wt.% CNFs (*c*, *d*), 40 wt.% MCFs (70 μm) (*e*, *f*), 40 wt.% MCFs (200 μm) (*g*, *h*), 40 wt.% CCFs (2 mm) (*i*, *j*).

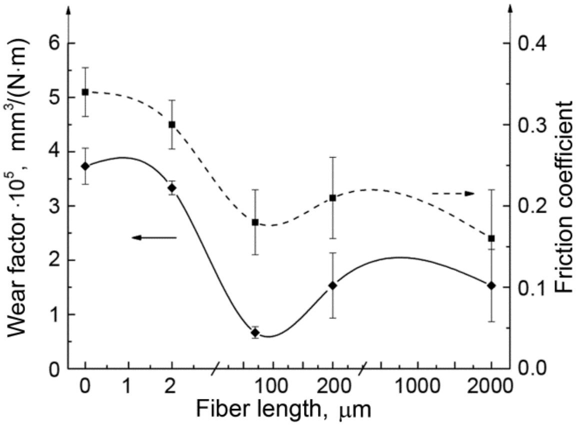

Fig. 4. Wear factor and friction coefficient of PPS and their composites versus carbon fiber size.

conditions of powder mixture preparation. This could be also accompanied by agglomeration of nanofibers (Fig. 3*d*). On the other hand, a comparable size of the polymer powder particle and the MCF length implies their uniform distribution in the PPS-matrix (Fig. 3*e*, *g*, *i*). High adhesion of micro- and millimeter CFs to the matrix in the reinforced composites is accompanied by their excellent mechanical characteristics (Table 1).

In this study we investigated tribological properties of PPS-composites filled with CFs of different dimensions. Fig. 4 presents the wear intensity and friction coefficient data as a function of the carbon fiber length. The data clearly suggest that the most efficient filler, in terms of increasing the wear resistance and decreasing the friction coefficient, is if MCFs with the fiber length ≈ 70 μm. The authors attribute this to an improvement of the reinforcement efficiency with the increasing CF length. As a result of efficient reinforcement, when a steel counterpart is in a friction contact with the surface of a high-strength PPS-composite, the former fractures and the products of its fracture additionally

TABLE 2. Physical-Mechanical Properties of UHMWPE-based Composites with Carbon Fibers

Filler content, wt.%	Density ρ, g/cm^3	Shore D density	Elastic/Elastic modulus E, GPa	Ultimate tensile strength σ_{UTS}, MPa	Elongation at break ε, %	Crystallinity degree χ, %
UHMWPE	0.93	57.5 ± 0.1	0.71 ± 0.04	42.9 ± 3.1	485 ± 28	56.5
0.5% CF	0.93	58.0 ± 0.1	0.72 ± 0.05	36.4 ± 2.5	398 ± 40	51.1
10% MCF (70 μm)	0.97	58.68 ± 0.4	0.97 ± 0.06	35.6 ± 2.2	397 ± 36	40.8
10% MCF (200 μm)	0.97	59.8 ± 0.2	1.13 ± 0.12	36.5 ± 3.5	394 ± 36	32.1
10% CCF (2 mm)	0.97	61.0 ± 0.3	1.67 ± 0.17	33.8 ± 2.9	279 ± 29	34.4

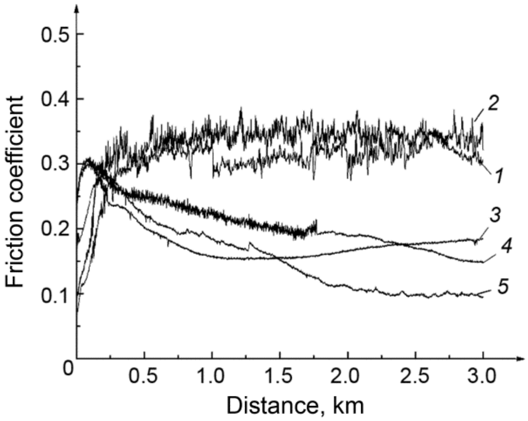

Fig. 5. Temporal variation of PPS friction coefficient (Curve *1*) and its composites with 0.3 wt.% CNFs (Curve *2*); 40 wt.% MCFs (70 μm) (Curve *3*); 40 wt.% MCFs (200 μm) (Curve *4*); 40 wt.% CCFs (2 mm) (Curve *5*).

stimulate microabrasive wear (Fig.3*h*, *j*). The 70 μm MCFs have an aspect ratio comparable to those of powders, therefore they can foster the formation of a third body from the wear debris, both decreasing the friction coefficient (Figs. 4 and 5) and protecting the polymer surface from wear (Fig. 3*f*).

Therefore, when designing PPS-composites for structural and tribotechnical applications a reasonable solution is a high degree of their loading with MCFs of lengths not shorter than 100 μm. An introduction of CFs via modification of the polymer matrix structure (actually dispersion hardening) increases the elastic modulus (Table 1) but does not practically change the tribological properties. Loading with CFs of a length of hundreds of micrometers due to reinforcement/hardening considerably deteriorates the tribological properties and, among other things, wears the steel counterpart out. It is therefore reasonable to fill PPS with solid-lubricant (polymer) particles not causing any dispersion hardening effect.

There is a different scenario of the effect of CF length on mechanical and tribological properties of carbon composites on UHMWPE. In the preparation of mixtures for sintering compression fine powder is used. This allows forming spherolite supermolecular structure during hot compression with a more uniform, compared to PPS, filler (fiber) distribution in the matrix. Table 2 lists mechanical properties of UHMWPE-based composites with carbon fibers of the same size as for PPS compositions. It should be specially mentioned that the degree of filling with MCF and CCF was reduced by a factor of 4, which is related to a low melt flow index of UHMWPE and an impossibility of forming heterogeneous composite structure in the case of a large fiber filler content.

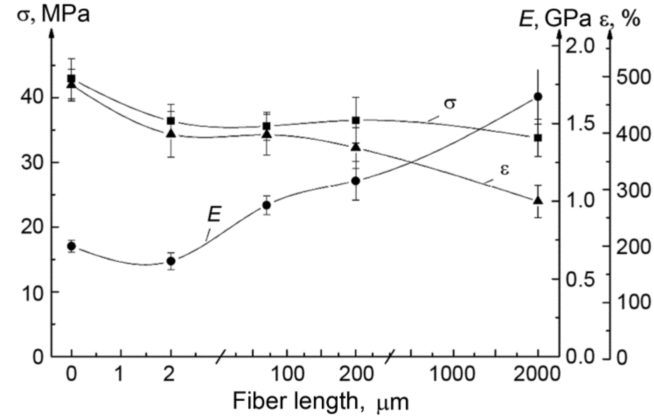

Fig. 6

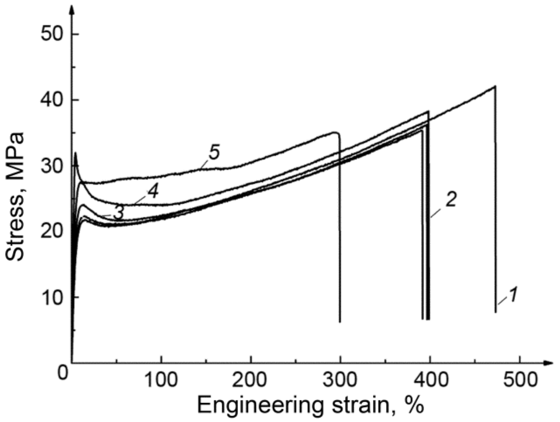

Fig. 7

Fig. 6. Mechanical properties of UHMWPE and its composites versus carbon fiber size.

Fig. 7. Stress-strain curves for PPS (Curve *1*) and its compositions with 0.3 wt.% CF (Curve *2*); 10 wt.% MCFs (70 μm) (Curve *3*); 10 wt.% MCFs (200 μm) (Curve *4*); 40 wt.% CCFs (2 mm) (Curve *5*).

One can see that similarly to PPS the strength properties increase with the CNF length. As expected, the deformation characteristics are observed to decrease. In particular, the ultimate tensile strength and elongation at break decrease by up to 1.2–1.7, remaining at considerably high levels. Figures 6 and 7 present the curves of dependence of mechanical properties of the UHMWPE-based carbon composites on the CF length. It is seen that due to the absence of adhesion a noticeable increase in the elastic modulus and ultimate tensile strength could be achieved for CCFs only in the case where the fibers pierce several spherolites (and their boundaries) simultaneously.

The investigations of supermolecular structure of UHMWPE-based carbon composites demonstrated that the this structure is retained up to an MCF filler content in the matrix of 10 wt.% (Fig. 8) [17]. It should be noted that the size of spherolites decreases, and there is no adhesion between the matrix and the CF. Therefore an increase in the fiber size is accompanied by a decrease in the size of spherolites and degree of crystallinity (Table 2), without any disturbance of the fiber distribution in the matrix.

We investigated tribological characteristics of UHMWPE-based composites with different CF lengths. Figure 9 presents the data on wear intensity and friction coefficient versus fiber length. It is clear that CNFs are most efficient in terms of improving wear resistance and CCF are slightly less efficient. The lowest friction coefficient is observed in a UHMWPE + 0.5 wt.% CNF composite: it is twice lower than in neat UHMWPE (Figs. 9 and 10). In MCF-filled composites (70 and 200 μm) the friction coefficient is higher than in an unfilled polymer. In a UHMWPE + 10 wt.% CNF composite the friction coefficient is a factor of 1.8 lower compared to the neat UHMWPE. The authors believe that MCFs are more chaotically oriented in the polymer matrix and, protruding above the friction surface, they actively hamper the motion of the steel counterpart (Fig. 8*f*, *h*). CCFs on the surface of tribocontact are imbedded into the polymer matrix ensuring its reinforcement. The absence of chemical bonding (adhesion) does not exert any essential counter-slipping action on the metal counterpart (Fig. 8*j*).

Wear intensity of UHMWPE varies as a function of CNF length in a similar manner (Fig. 9). Nanofibers after their introduction (wear resistance increases by a factor of 2.7) perform the role of a solid-lubricant medium due to the absence of adhesion [17]. Long carbon fibers (CCF) withstand the compressive and shearing loading from the counterpart, protecting the surface of tribocoupling from intensive wear (wear resistance increases twice). The results on wear resistance of UHMWPE-based composites filled with fibers of different lengths are consistent the observed wear track surface patterns (Fig. 8). Note that the wear track surface roughness is lowest in the UHMWPE + 0.5 wt.% CNF nanocomposite, Fig. 8*d*.

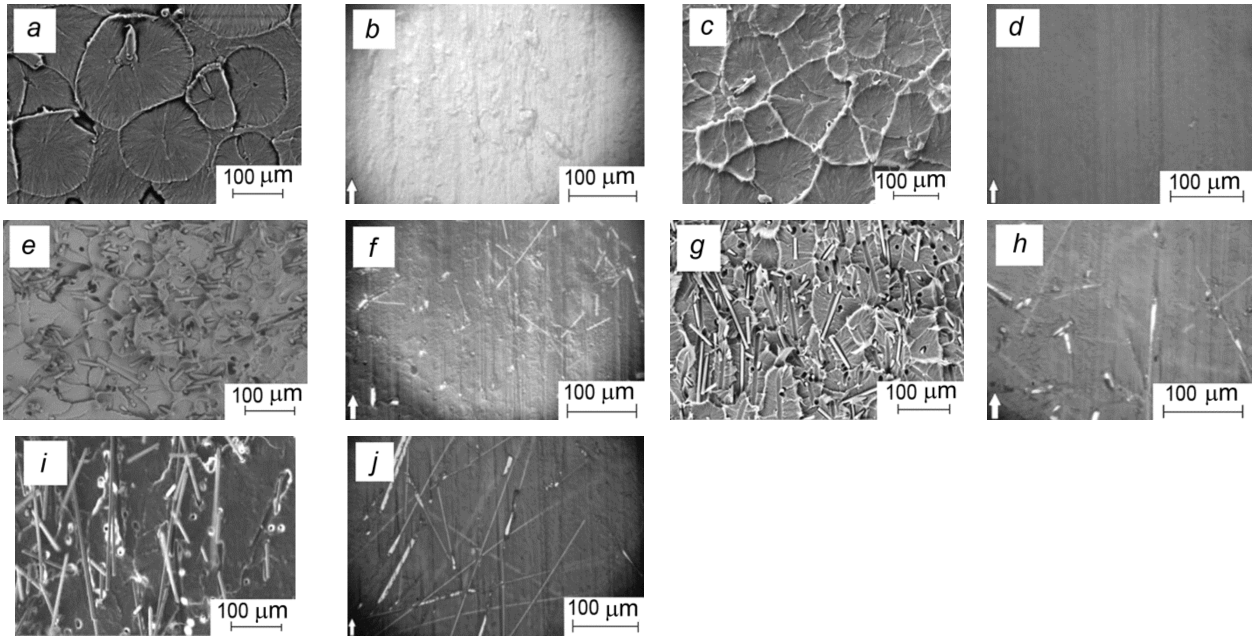

Fig. 8. Supermolecular structure and optical micrograps of wear track surfaces of UHMWPE (*a*, *b*) and its composites with 0.5 wt.% CNFs (*c*, *d*); 10 wt.% MCFs (70 μm) (*e*, *f*); 10 wt.% MCFs (200 μm) (*g*, *h*); 10 wt.% CCFs (2 mm) (*i, j*).

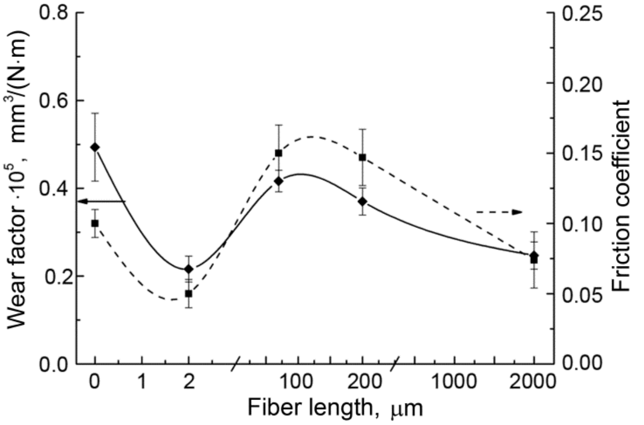

Fig. 9

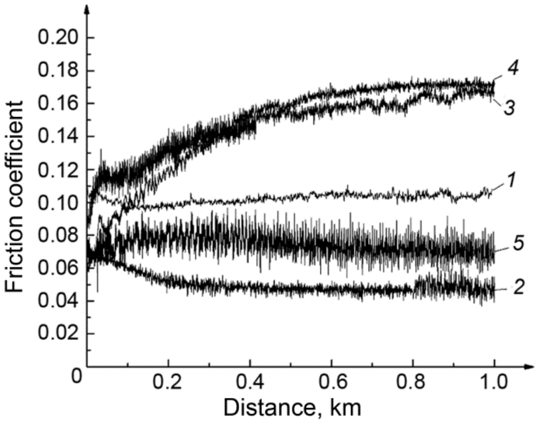

Fig. 10

Fig. 9. Wear intensity and friction coefficient of UHMWPE and its composites versus carbon fiber length.

Fig. 10. Friction coefficient of UHMWPE (Curve *1*) and its composites with 0.5 wt.% CNFs (Curve *2*); 10 wt.% MCF (70 μm) (Curve *3*); 10 wt.% MCFs (200 μm) (Curve *4*); 10 wt.% CCFs (2 mm) (Curve *5*).

Thus, the elastic modulus in carbon composites based on an nonpolar UHMWPE-matrix due to low adhesion at the filler content of 10 wt.% can be improved up to a factor of 1.8 by loading with CFs in the millimeter range. Nanofibers, due to low adhesion, modify the polymer matrix rather weakly, but act as a solid-lubricant medium in dry sliding friction. A combined loading with CFs of two sizes (nano- and millimeter) can ensure high mechanical and tribological properties of UHMWPE composites [18].

SUMMARY

In this study a comparison of the effect of carbon fiber dimensions on mechanical and tribological properties of carbon composites based on matrices differing in their physical-chemical nature (PPS, UHMWPE) has been performed.

It has been shown that the supermolecular structure formed during sintering compression in thermoplastic PPS and UHMWPE polymers different in nature determines the distribution of different-size carbon fibers in the matrix and, as a result, the level of tribological characteristics. Composites of structural/tribotechnical applications based on a high-strength PPS-matrix can be formed at a high degree of loading (40 wt.%) with 70 µm-long MCFs. An increase in wear resitance occurs via the formation of a third body from the wear products, which reduces the friction coefficient. Filling of a PPS polymer matrix with nanofibers modifies its structure via the mechanism of dispersion hardening and is not accompanied by an increase in tribological properties. Loading of PPS with CCFs having lengths of units of millimeter effectively strengthens the material but considerably worsens tribological properties. For antifriction applications, the most efficient fibers in PPS-composites were (milled) microfibers of an average size of 70 µm (wear resistance increases by a factor of 5, friction coefficient decreases by a factor of 1.7). Composites for structural-tribological applications based on UHMWPE-matrix filled with 10wt.% carbon fibers are manufactured by a uniform distribution of CCFs in the polymer matrix and a simultaneous loading with carbon fibers. In terms of increasing wear resistance, the most effective fillers for the UHMWPE-matrix with a spherolite supermolecular structure are the carbon nanofibers acting as solid lubricants (wear resistance increases by a factor of 2.7, friction coefficient decreases twice). Carbon micro- and millimeter long fibers (70 µm, 200 µ, 2 mm) reinforce the polymer composition, opening prospects for designing multi-component, high-strength solid-lubricating carbon composites on an ultra-high-molecular-weight PE matrix for their practical applications in tribotechnical units of machines and mechanisms under different operating conditions.

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