

EFFECT OF THE MATRIX STRUCTURE ON THE TRIBOLOGICAL PROPERTIES OF SOLID-LUBRICANT COMPOSITES BASED ON HIGH-TEMPERATURE POLYIMIDE THERMOPLASTICS

S. V. Panin, J. Luo, D. G. Buslovich, V. O. Alexenko, and L. A. Kornienko

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The structure, the mechanical characteristics and the tribological properties of polyimide (PI)- and polyetherimide-(PEI) based composites, differing by the presence of 'hinged' oxygen atoms in the polymer molecular chain, are studied. The composites are reinforced with chopped carbon fibers and simultaneously loaded with organic (PTFE) and inorganic (MoS_2) solid lubricant fillers. The tribological tests are carried out according to the ball-on-disk scheme under dry sliding friction on a ceramic counterface in the temperature range of $T = 23\text{--}180^\circ\text{C}$. It is shown that only the PEI/10% CF/10% PTFE composite possesses the highest wear resistance in the entire experimental temperature range. At the same time, loading with PTFE particles ensures the formation of a stable layer (transfer film) of the secondary structures and its adherence to the sliding surface of the polymer composite, thus protecting it from wear. The changes in wear rate and friction coefficient are well correlated with each other. In the case where a MoS_2 solid lubricant filler is loaded, the transfer film is fixed on the composite sliding surface only at the highest test temperature $T = 180^\circ\text{C}$, which is due to the presence of oxygen atoms in the PEI molecules. This provides a low coefficient of friction and a relatively high wear resistance to the PEI/10 CF/10 MoS_2 ternary composite. A comparative analysis of the tribological properties of the two types of polymer matrices have shown that the wear rate of the PEI-based composites loaded with PTFE is equally low at $T = 23^\circ\text{C}$ and 120°C , while at $T = 180^\circ\text{C}$ it is 300 times lower than that of the PI-based materials. This is thought to be due to the fact that a 'more rigid' PI matrix (without any hinged units in the macromolecule) is incapable of confining the solid PTFE lubricant in the transfer film layer under conditions of a high oscillating friction coefficient. The PEI-based composites are recommended for use in tribounits due to both high manufacturability governed by the polymer chain flexibility and high wear resistance due to the formation of stable secondary structures (transfer film) on the sliding surfaces in the temperature range of $T = 23\text{--}180^\circ\text{C}$.

Keywords: polyimide, polyetherimide, carbon fibers, polytetrafluoroethylene, molybdenum disulfide, elastic modulus, friction coefficient, wear, transfer film.

INTRODUCTION

Polyimides (PIs) belong to a class of structural materials with a harmonic combination of such valuable physical-mechanical and functional properties as high-temperature stability, heat resistance, fire resistance, chemical inertness, radiation resistance, strength and high elasticity modulus, as well as survivability in a wide temperature range [1–5]. They are now being used in such advanced industries as aircraft engineering, aerospace, electrical engineering, electronics, transport engineering and other branches. Most PIs, exhibiting an exceptionally high service performance

Institute of Strength Physics and Materials Science of the Siberian Branch of the Russian Academy of Sciences, Tomsk, Russia, svp@ispms.ru; jiangkun169@gmail.com; buslovich@ispms.ru; vl.aleksenko@mail.ru; rosmc@ispms.ru. Translated from *Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika*, No. 3, pp. 123–130, March, 2022. Original article submitted January 20, 2022.

ТАБЛИЦА 1. Composition of Experimental Materials

No.	Filler content, wt. %	Notation
1	PI	PI
2	PI +10% CF	PI/10CF
3	PI +10% CF +10% PTFE	PI/10CF/10PTFE
4	PI +10% CF +10% MoS ₂	PI/10CF/10MoS ₂
5	PEI	PEI
6	PEI +10% CF	PEI/10CF
7	PEI +10% CF +10% PTFE	PEI/10CF/10PTFE
8	PI +10% CF +10% MoS ₂	PEI/10CF/10MoS ₂

close to the maximum achievable values for organic materials, possess a significant deficiency – a difficulty of processing into bulk products due to a strong intermolecular interaction and a high rigidity of the polymer chains. The design of PI-based composites, combining their manufacturability by the industrial methods with the maintained high basic service characteristics, is an urgent task. A paradigm shift in the polyimide material engineering is the development of polyetherimide (PEI) thermoplastics, manufactured by an introduction of the hinged oxygen atoms into the recurring units composed of aromatic and heterocyclic fragments [6, 7]. Furthermore, despite the increased flexibility of the polymer chain, the basic properties of polyimides – their excellent physical-mechanical characteristics and high decomposition onset temperature are retained.

Heat-resistant PIs and PEIs rank high among the structural thermoplastics along with polyethersulfone, polyetheretherketone, polyphenylene sulfide, etc. [8–10]. It is to be noted that an increased flexibility of the main polymer chain and/or a decrease in the intermolecular forces opened up new prospects of PEI applications in the production of filled composite materials [11–15]. The retention of advanced mechanical properties in a wide range of temperatures is attractive for the designers of new polymer composites, and in terms of antifriction applications is promising for fabrication of the friction unit components. A solution to this problem is achieved, among other things, by an introduction of solid lubricant fillers (polytetrafluoroethylene, PTFE [16, 17], graphite (Gr) [18], molybdenum disulfide (MoS₂) [19] and a number of other compounds, offering a decrease in friction coefficient and wear under dry friction.

In this work our task is to study the tribological characteristics of PT- and PEI- based high-strength antifriction composites of differing molecular structures [20] in a wide temperature range of $T = 23\text{--}180^\circ\text{C}$. This would allow determining and validating the acceptable service conditions of the proposed antifriction composites relying on the commercial grades of PIs and PEIs, aimed at their application in the tribological units.

EXPERIMENTAL MATERIAL AND PROCEDURE

The samples were fabricated from PI (Solver PI-Powder 1600, China) and PEI powders (Solver PEI ROOH, China) with the average particle size of 16 μm , the fillers were: i) fine-grained FLURALIT powder produced by a thermal decomposition of PTFE-4 ($\varnothing \sim 3 \mu\text{m}$) (Fluralit Sintez LLC, Russia); ii) molybdenum disulfide MoS₂ ($\varnothing 1\text{--}7 \mu\text{m}$) (Climax Molybdenum, USA). The fibers were chopped carbon fibers (CFs) (Tenax®-A) with of $l \sim 2 \text{ mm}$ (aspect ratio of ≈ 100). Table 1 presents the compositions of the experimental materials.

The PI and PEI powders were mixed in an MP/0.5*4 planetary ball mill (Techno-Center LLC, Rybinsk), with a preliminary dispersion of the components in a PSB-Gals 1335-05 ultrasonic bath (TSUO PSB-Gals, Moscow). The bulk samples of the polymer composites were hot pressed from the powder mixtures at a pressure of 15 MPa and a temperature of 370°C in a laboratory setup based on an MS-500 hydraulic press (NPK TekhMash LLC, Moscow), equipped with a ring-shape furnace (ITM LLC, Tomsk). After sintering, the work pieces were cooled without removing the load at a cooling rate of $\Delta T = 2^\circ\text{C}/\text{min}$.

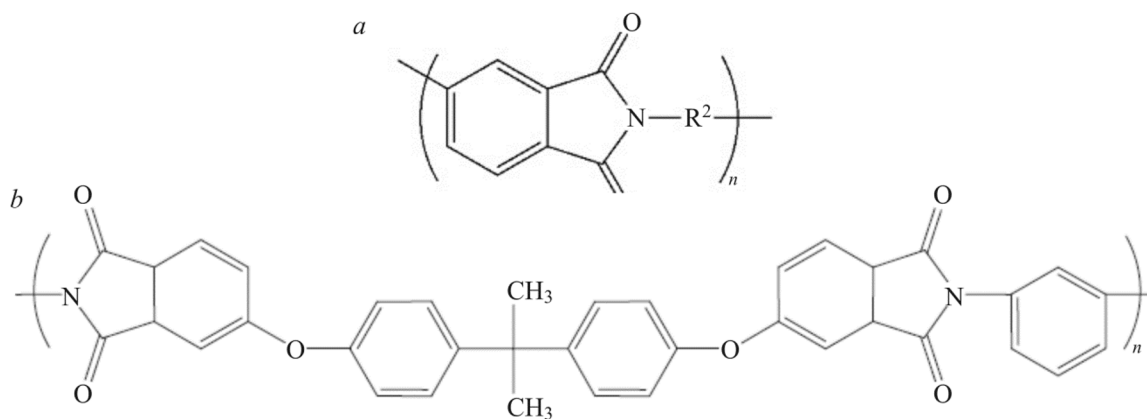


Fig. 1. Chemical structure of aromatic polyimide (a) and polyetherimide (b).

The Shore D hardness was determined in an Instron 902 hardness tester. The mechanical characteristics of the dog-bone specimens were obtained in the uniaxial tensile tests in an Instron 5582 electromechanical universal testing machine. The wear tests were performed in a dry friction sliding mode according to the ball-on-disk scheme in a TNHT-S-BE-0000 high-temperature nanotribometer (CSEM) at a load of 5 N and a sliding velocity of $V = 0.3$ m/s. The radius of the counterface shaped as an Al₂O₃ ceramic ball was 6 mm. The testing distance was – 1 km, the tribotrack trajectory radius – 16 mm.

The surface topography of the tribotacks was examined in a Neophot 2 optical microscope (Carl Zeiss Jena, Germany), equipped with a Canon EOS 550D digital camera (Canon Inc.), and in an Alpha-Step IQ contact profilometer (KLA-Tencor). The structural studies were carried out in a LEO EVO 50 scanning electron microscope (Carl Zeiss, Germany) with an Oxford INCA X-Max80 EDS microanalysis system at an accelerating voltage of 20 kV on the rupture surface of the specimens cooled in liquid nitrogen.

The crystallinity of both polymers was determined in an XRD-6000 diffractometer (Shimadzu) using CuK_α-radiation. Figure 1 presents the chemical structure of PI and PEI specimens.

RESULTS AND DISCUSSION

Table 2 presents the physical-mechanical properties of PI- and PEI based composites. It is evident that an addition of 10% of chopped CFs noticeably increases the key mechanical characteristics of PI- and PEI composites: the elasticity modulus increases twice, and the yield strength – by a factor of 1.2. A subsequent introduction of solid lubricant particles into the PI/CF and PEI/CF binary mixtures slightly decreases the strain-strength property indices. The mechanical characteristics of the initial PEI (elasticity modulus, yield strength, elongation at break) exceed those of PI by about 10%, which might be due to a higher crystallinity of the former (32 vs 21%). In the composites based on these polymers, the differences in mechanical characteristics are compensated for by the CF reinforcing action. The elongation in tension of all experimental composites has decreased by 4–5 factors, and their fracture pattern was brittle.

Figure 2 presents SEM micrographs of the structure of PI- and PEI based composites. It is seen in Fig. 2a, e that the reinforcing fibers are distributed quite homogeneously over the bulk. Furthermore, the solid lubricant PTFE and MoS₂ fillers are also located in the CF-reinforced polymer matrix in a quite homogeneous fashion and show no signs of agglomeration (Fig. 2b, c and e, f). Thus, a similarity between the forming structures of ternary composites based on PI- and PEI matrices correlates with the similarity of their mechanical characteristics. Note that the matrix material in them differs by the presence of a central link in the PEI molecular chain, which is bound via the hinged oxygen atoms (Fig. 1).

We performed tribological tests of the experimental composites within the temperature interval of 23–180°C (Fig. 3). The data in Fig. 3 suggest the following:

TABLE 2. Physical-Mechanical Properties of PI-Based Composites

No.	Composition	Density ρ , g/cm^3	Shore D hardness	Elasticity modulus E , GPa	Yield strength σ_{UTS} , MPa	Elongation at break ϵ , %
1	PI	1.37	80.2± 0.8	2.60±0.69	110.7±1	13±0.7
2	PI/10CF	1.42	80.6±0.4	6.40±0.33	152.1±6.4	5.9±0.3
3	PI/10CF/10PTFE	1.44	77.5±0.6	5.79±0.45	115.9±10.8	4.1±0.3
4	PI/10CF /10MoS ₂	1.51	82.0± 0.3	6.06±0.32	113.1±9.1	3.0±0.1
5	PEI	1.26	79.9±0.3	3.12±0.15	123.1±0.5	16.1±1.2
6	PEI/10CF	1.31	81.4±0.3	6.54±0.43	153.2±12.5	3.7±0.6
7	PEI/10CF/10PTFE	1.36	79.0±0.3	6.17±0.26	117.3±8.0	3.1±0.3
8	PEI/10CF/10MoS ₂	1.41	81.9± 0.1	6.26±0.17	121.0±5.0	3.5±0.3

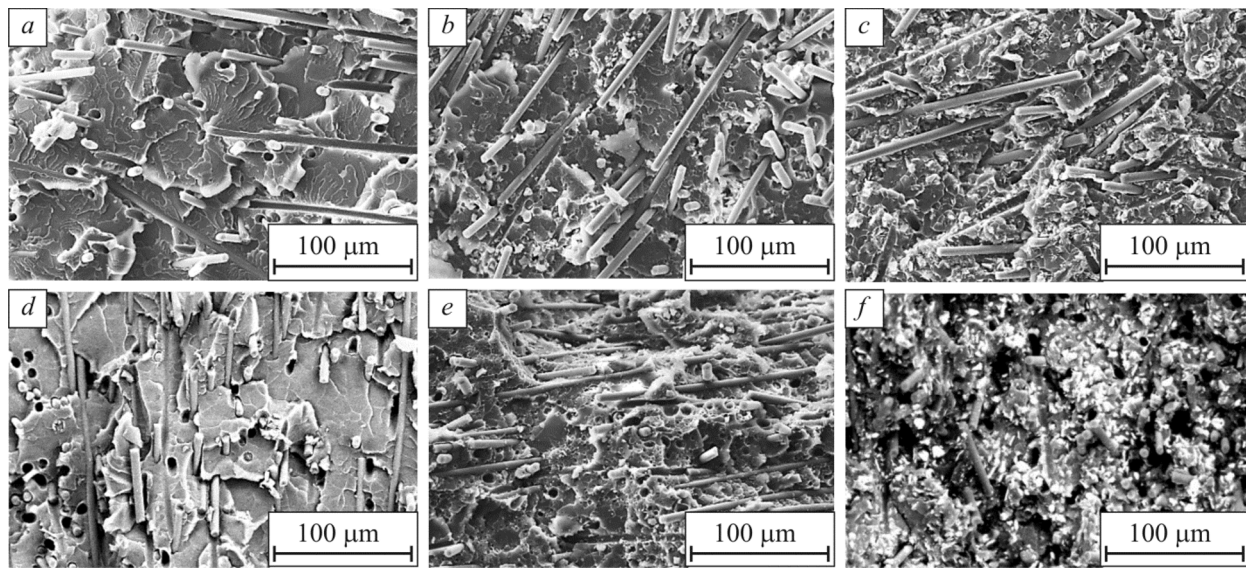


Fig. 2. SEM micrographs of the composites: PEI/10CF (a), PEI/10CF/10PTFE (b), PEI/10CF/10MoS₂ (c) and PI/10CF (d), PI/10CF/10PTFE (e), PI/10CF/10MoS₂ (f).

– compared to the PI-based composites, the friction coefficients of PEI/10CF/10PTFE composites are twice lower at $T = 23^\circ$ ($\mu = 0.048$ vs $\mu = 0.094$) and nearly three times lower at $T = 180^\circ\text{C}$; at $T = 180^\circ\text{C}$ the wear rate in PEI composites is 300 times lower than that of PI composites;

– as the test temperature is increased, the change of the friction coefficient in PI/10CF/10PTFE is not proportional to the increasing wear rate; a similar behavior but with a different trend characterizes the PEI/10CF/10PTFE composite;

– the presence of MoS₂ in PI/10CF/10MoS₂ does not ensure the formation of secondary structures and their adherence on the sliding surface, which protect the surface from wear (composite wear rate at $T = 180^\circ\text{C}$ is 15 times higher than that of the PEI-based composites).

In our earlier work [21], we demonstrated that the wear rate and friction coefficients of the PI/CF/solid lubricant fillers are determined by the formation of a transfer film on the counterface and, more importantly, of the secondary structures on the sliding surface of the composite. Figure 4 presents the variation of the friction coefficients in time at three experimental temperatures. The high values and oscillating character of the friction coefficient variation

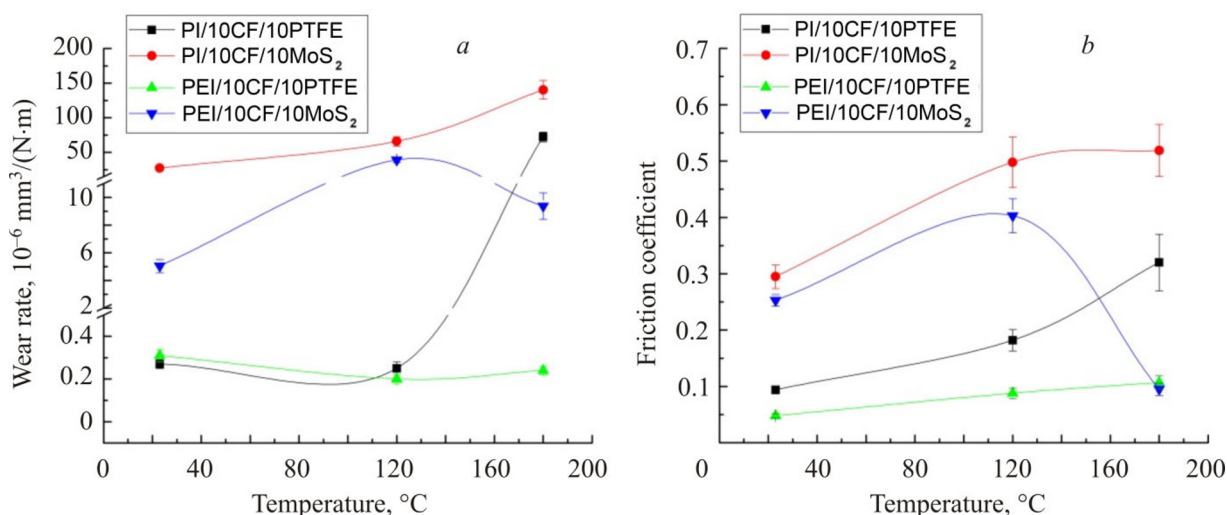


Fig. 3. Tribological characteristics of PI- and PEI-based composites.

in the PI/10CF/10PTFE composite at elevated temperatures ($T = 120$ and 180°C) are due to both the thermally induced increase of the friction coefficient of the polymer matrix material itself and the secondary structure formation instability on the sliding surface (Fig. 4b, c). In the case of PI/10CF/10MoS₂, the friction coefficient even at room temperature has the value of $\mu = 0.3$ and even increases further (Fig. 4d–f). This suggests that MoS₂ particles do not act as a solid lubricant for this polymer matrix type.

In the case of the PEI matrix, an increase in the test temperature is also followed by a higher amplitude of the friction coefficient oscillations; however, in PEI/10CF/10PTFE its average value in the entire interval of the experimental temperatures is found to be $\mu \approx 0.1$ (Fig. 4g–j); in PEI/10CF/10MoS₂ the friction coefficient value increases with the temperature, similarly to the case of the PI composite, however, at $T = 180^\circ\text{C}$ at the end of the wear-in stage it sharply decreases and remains at a level of $\mu \approx 0.1$ (Fig. 4k–l).

For the sake of illustration of the formation of secondary structures on the sliding surface, which determine the wear resistance of the ceramic–polymer mating in terms of compositions, Table 3 presents the EDS microanalysis results. The regions where the EDS data were obtained are shown on the respective SEM micrographs of the surfaces of the wear tracks (Fig. 5).

As shown above, the most efficient solid lubricant filler is PTFE. In the case of PI/10CF/10PTFE, it ensures high tribological properties at the temperatures up to 120°C , and in the PEI/10CF/10PTFE composite – up to $T = 180^\circ\text{C}$. In both cases, the PTFE transfer film provides the formation of smooth sliding surfaces, which could be interpreted as the formation of secondary structures (Fig. 5a, c). It is important that the secondary-structure layer formed during friction across the PEI/10CF/10PTFE composite is retained within the entire test temperature interval of $T = 23$ – 180°C .

We believe that a sharp increase of the wear rate in the PI/10CF/10PTFE composite at $T = 180^\circ\text{C}$ is due to the fact that a more ‘rigid’ PI matrix (not containing any hinged links in the macromolecule) under the conditions of high oscillating friction coefficient is incapable of adhering the solid-lubricant PTFE-containing layer (Fig. 5a).

The solid-lubricant MoS₂ filler in fact failed to fulfill its function, except for the case of the PEI composite at $T = 180^\circ\text{C}$. Furthermore, the wear in the PI/10CF/10MoS₂ composite was noticeably higher than in PEI/10CF/10MoS₂ in the entire experimental temperature interval. An increase in ‘severity’ of the tribotest conditions due to a high temperature of $T = 180^\circ\text{C}$ favored adhering of MoS₂ to the sliding surface of the composite due to the presence of oxygen atoms in the PEI molecule. As a result, the friction coefficient decreased and the secondary-structure layer protected the ternary PEI/10CF/10MoS₂ composite from wear. Note that compared to a similar PI-based composite the wear rate increased by a factor of 15 only, which ensured a certain visual similarity to the layer of secondary structures on its sliding surface (Fig. 5b, d).

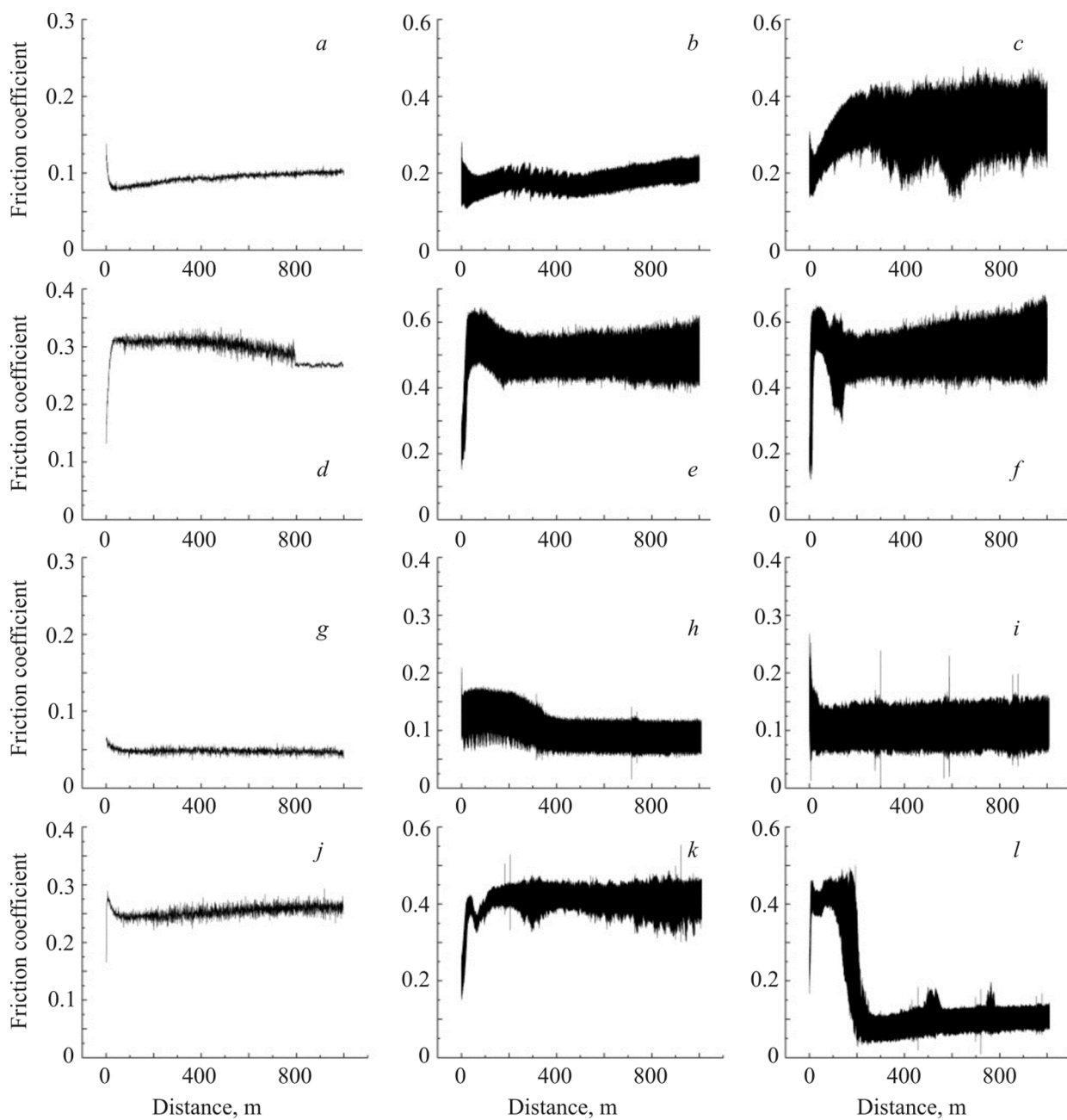


Fig. 4. Time dependence of the friction coefficient of PI/10CF/10PTFE (*a, b, c*), PI/10CF/10MoS₂ (*d, e, f*) and PEI/10CF/10PTFE (*g, h, i*), PEI/10CF/10MoS₂ (*j, k, l*), 23°C – *a, d, g, j*, 120°C – *b, e, h, k*, 180°C – *c, f, i, l*.

TABLE 3. Results of EDS-Analysis of Film on Wear Surfaces of Composite Samples Presented in Fig. 5. Test Temperature 180°C

Element	Spectrum 1 at.%	Spectrum 2 at.%	Spectrum 3 at.%	Spectrum 4 at.%	Spectrum 5 at.%
PI/10CF/10PTFE					
C	55.60	89.76	92.69	57.93	58.13
O	31.84	7.44	5.16	23.46	38.06
F	12.56	2.80	2.15	18.61	3.82
PI/10CF/10MoS ₂					
C	67.82	69.40	74.38	82.97	73.83
O	24.23	24.17	17.36	11.47	15.12
S	6.39	5.32	6.37	4.70	9.23
Mo	1.57	1.10	1.89	0.85	1.81
PEI/10CF/10PTFE					
C	43.93	61.55	62.23	61.72	65.49
O	12.38	22.17	27.55	18.31	21.45
F	43.69	16.28	10.22	19.97	13.06
PEI/10CF/10MoS ₂					
C	77.24	69.45	70.40	68.68	82.17
O	8.90	26.54	26.39	9.95	14.69
S	9.67	2.65	2.16	15.08	2.10
Mo	4.19	1.36	1.04	6.30	1.05

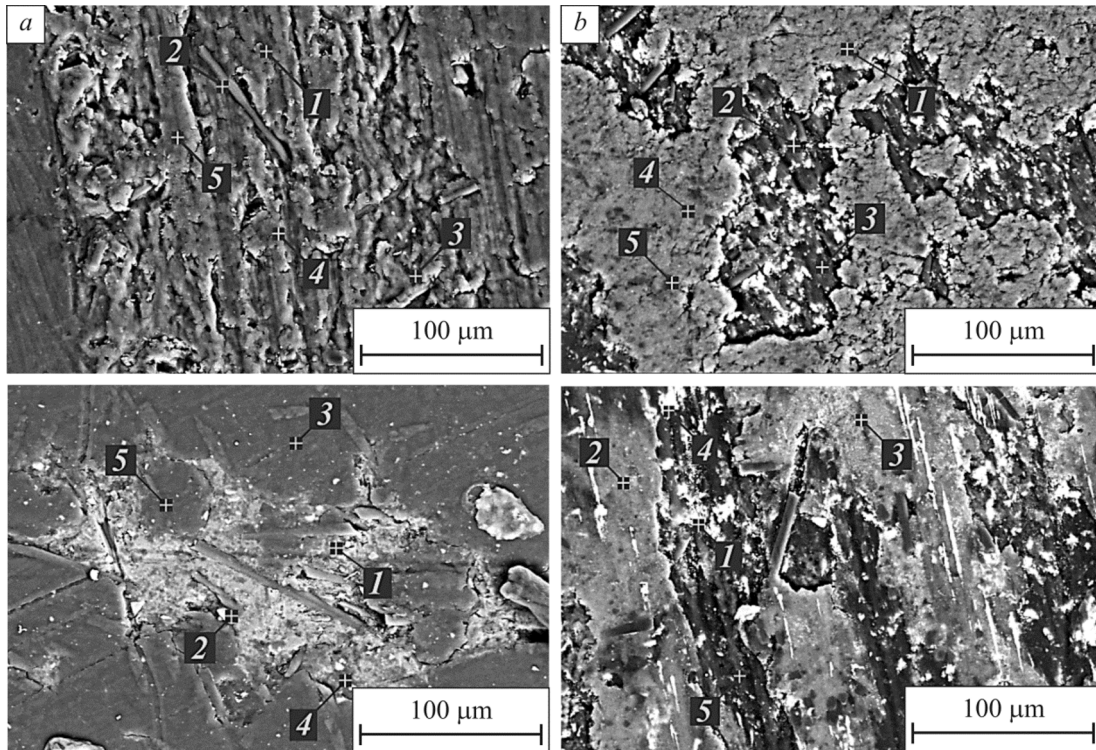


Fig. 5. SEM micrographs of wear surfaces under friction: PEI/10CF/10PTFE (a), PI/10CF/10MoS₂ (b), PEI/10CF/10PTFE (c), PEI/10CF/10MoS₂ (d). Test temperature 180°C.

CONCLUSIONS

The structure and the mechanical and tribological characteristics (in the temperature interval of 23–180°C) of polyimide- and polyetherimide-based composites, differing by the presence of ‘hinged’ oxygen atoms in the molecular chain of the latter have been studied. The composites were reinforced by long carbon fibers, with the solid-lubricant particles being PTFE and MoS₂. It has been shown that the presence of 10 wt.% of 2 mm-long reinforcing carbon fibers provides a nearly twofold increase of the elasticity modulus and an approximately 1.5-times increase of the yield strength, irrespective of the matrix material.

A comparative analysis of tribological properties of the ternary PEI- and PI-based composites has been performed and it has been shown that at $T = 180^{\circ}\text{C}$ the wear rate of PEI-based composites is 300 times lower than that in the PI-based composites. The highest wear resistance under the ball-on-disk test conditions in the entire experimental temperature range of 23–180°C was demonstrated by the ternary PEI/10CF/10PTFE composite. Due to PTFE, a stable second-structure layer is formed of the sliding surface of the specimens. The wear rate and friction coefficient values in the experimental composites correlate well with each other in the entire range of temperatures studied in this work.

In the PI- and PEI-based ternary composites at the ball-on-disk tribotest parameters used in this work, the MoS₂ particles do not generally act as solid lubricating agents, but rather as finely dispersed reinforcing inclusions. We believe that this is due to the insufficient load level for their layer-by-layer fracture, followed by their adhering to the sliding surface. The transfer film (layer of secondary structures) is observed to adhere to the sliding surface of the polymer composite only at the test temperature of $T = 180^{\circ}\text{C}$ due to the presence of oxygen atoms in the PEI molecule. This gives rise to a sharp decrease of the friction coefficient and protects from wear. However, at $T = 180^{\circ}\text{C}$ the wear rate of the PEI/10CF/MoS₂ composite is by an order of magnitude higher than that in a similar PEI/10CF/10PTFE composite, which is due to their significant wear in the running in stage.

The PEI-based composites are recommended for applications in the triunits because of their high manufacturability (recyclability) due to the chain flexibility and high wear resistance by virtue of the formation of adhered (stable) secondary structures on the mating surfaces in the entire temperature interval of $T = 23\text{--}180^{\circ}\text{C}$.

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