

Effect of Irradiation on Interfacial Interaction and Structure Formation in Filled PTFE Composites

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Abstract—The supramolecular structure and tribological properties of filled polytetrafluoroethylene composites irradiated above the melting point of the crystalline phase of the polymer component and the phase transitions in them are investigated. In unirradiated composites, phase separation is observed, that is, the separation of the filler from the polymer matrix. The supramolecular structure of the polymer component does not depend on the nature and concentration of the filler, and it is characterized by the formation of lamellae during sintering and subsequent crystallization. Radiation exposure leads to the disappearance of the phase separation and the formation of axiolites with the radial orientation of fibrils, in the center of which the filler particles are located. Changes in the structure are explained by an increase in interfacial interactions through the radiation grafting of macromolecules (and low-molecular-weight products) to the surface of the filler particles. The linear wear rate of irradiated composites is 50 times lower relative to the unirradiated samples because of the transition from the delamination to abrasive wear mechanism.

Keywords: PTFE composites, supramolecular structure, radiation modification, electron microscopy, fibrils, lamellae, spherulites, axiolites, tribological properties

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INTRODUCTION

Polytetrafluoroethylene (PTFE) is widely used in various industries because of its exceptional chemical, thermal, and antifriction properties. The disadvantages of PTFE are related to its extremely low wear resistance to friction. Wear of the polymer is usually lowered through the creation of composites based on PTFE with a variety of dispersed particles (coke, graphite, carbon fiber, carbon glass, bronze, or molybdenum dioxide). The formation of composites decreases wear by two to three orders of magnitude compared with the initial, unfilled PTFE sample [1]. Chemical modification (copolymerization of tetrafluoroethylene with other monomers) is also used to improve the wear resistance [2], but can give no principal advantages in comparison with composites.

It is known that polymers are characterized by a strong dependence of the macroscopic properties on their supramolecular structure, and this dependence may appear even stronger than the dependence on the molecular (chemical) nature of the polymer [3, 4]. This fully applies to bulk PTFE composites, in which the concentration, size, shape, and interfacial interaction of filler particles and the polymer component may have a strong effect on structure formation and macroscopic properties. A change in the morphology of

the polymer component of PTFE under the effect of a filler has been reported in a number of studies [5, 6].

Recently, a method for the radiation-chemical modification of PTFE in the melt was developed, which reduces the rate of its wear by four to five orders of magnitude [7, 8]. The conclusion of [9, 10] is that a significant improvement in the macroscopic properties of PTFE is due to a global change in its morphology, that is, the transition from the lamellar to spherulitic supramolecular structure. Therefore, it was interesting to study the structural changes in the PTFE composites exposed above the melting temperature of the polymer component.

The goal of this work was to study the interfacial interactions and structure formation in PTFE composites irradiated above the melting point of the polymer matrix depending on the nature and concentration of the filler and the impact of these processes on the mechanism of wear.

EXPERIMENTAL

Objects. A wide range of heat-resistant PTFE composites were studied. They were prepared using conventional methods of dry blending and cold pressing followed by sintering at a temperature of 380°C. Inorganic and organic micro-sized powder particles (coke, graphite, bronze, molybdenum disulfide, cobalt

Table 1. Composition of the test PTFE composites

No.	Composite	Filler
1	F4KS2	Cobalt oxide, 2 wt %
2	F4K20	Foundry coke, 20 wt %
3	AFG80VS	Graphite, 20 wt %
4	F4UV15	Carbon fiber, 15 wt %
5	F4UV15M5	Carbon fiber, 15 wt %; MoS ₂ , 5 wt %
6	F4UV15M10	Carbon fiber, 15 wt %; MoS ₂ , 10 wt %
7	F4UV15G5	Carbon fiber, 15 wt %; graphite, 5 wt %
8	F4UV15G10	Carbon fiber, 15 wt %; graphite, 10 wt %
9	F4S15	Glass fiber, 15 wt %
10	F4Br40	Bronze, 40 wt %
11	F4Br40M2	Bronze, 40 wt %; MoS ₂ , 2 wt %
12	F4Br40M10	Bronze, 40 wt %; MoS ₂ , 10 wt %
13	F4Br40G5	Bronze, 40 wt %; graphite, 5 wt %
14	F4Br40G10	Bronze, 40 wt %; graphite, 10 wt %
15	F4Br60	Bronze, 60 wt %
16	F4Br40Sav5	Bronze, 40 wt %; carbon black, 5 wt %

oxide) and milled fibers (glass and carbon) were used as fillers. For the preparation of composites, we used a powder of high-molecular-weight PTFE of suspension polymerization ($MW \sim 5 \times 10^6$). The filler concentration was varied in the range of 2–60 wt %. The composition of the test composites is presented in Table 1. The size of the dispersed particles ranged from 10 to 50 μm . The fillers can be arbitrarily divided into two groups: those with low and high surface energy. Carbon fiber, coke, and graphite are in the group with low surface energy. Inorganic fillers such as cobalt oxide, molybdenum disulfide, bronze, and fiberglass have a high surface energy.

Irradiation. The samples were irradiated at $335 \pm 2^\circ\text{C}$ above the melting point of PTFE crystallites, which is 327°C , in an inert atmosphere (argon) with ^{60}Co γ -photons with a mean energy of 1.25 MeV with an absorbed dose rate of 5 kGy/h. The radiation dose was 200 kGy.

High-resolution electron microscopy. The supramolecular structure of the composites was examined by high-resolution scanning electron microscopy (HRSEM). The objects of research were prepared in liquid nitrogen in order to obtain cleavages. To obtain images, a JSM-7500F scanning electron microscope with a field-emission cathode (JEOL, Japan) was employed. Images were obtained in the low-energy secondary-electron mode, as this mode ensures the highest resolution: at a primary beam energy of 5 keV, the resolution was 1 nm. In order to avoid charging effects or the destruction of objects under the action of the electron probe, the following approaches were used: (i) the investigation was carried out at a low elec-

tron-probe current (3×10^{-11} A), which was set using a field-emission cathode with cold field emission, and (ii) a platinum metal film of approximately 5 nm in thickness was applied to the cleavage surface by magnetron sputtering.

The chemical composition of the test composites was monitored by X-ray microanalysis (XMA). For this purpose, we used an INCA Penta FETx3 energy-dispersive analyzer (OXFORD, United Kingdom) which was supplied as part of the scanning electron microscope.

Calibration was carried out at a probe energy of 5 keV using a high-purity silicon crystal. In determining the chemical composition, the scan area varied from 2.5×2.5 to 200×150 μm .

Thermal analysis. Thermograms of melting–crystallization of the composites were investigated by differential scanning calorimetry (DSC) using a DSC 204 F1 Phoenix instrument (NETZSCH) at a scan rate of $5^\circ\text{C}/\text{min}$. During the entire time of scanning, the samples were under helium at a flow rate of 25 mL/min. The points of melting or crystallization were determined by the maximum intensity of the peaks. The enthalpy of melting and crystallization was calculated using the linearly proportional dependence of the enthalpy on the area under the peaks in the thermograms.

Tribological tests. The tribological properties were investigated using a UMT-3 tribometer (CETR, United States). Tests were carried out according to a kinematic pin-on-disc pattern under conditions of dry friction at a contact pressure of 5 MPa and a disc sliding rate relative to a fixed sample of 1 m/s. A disc made

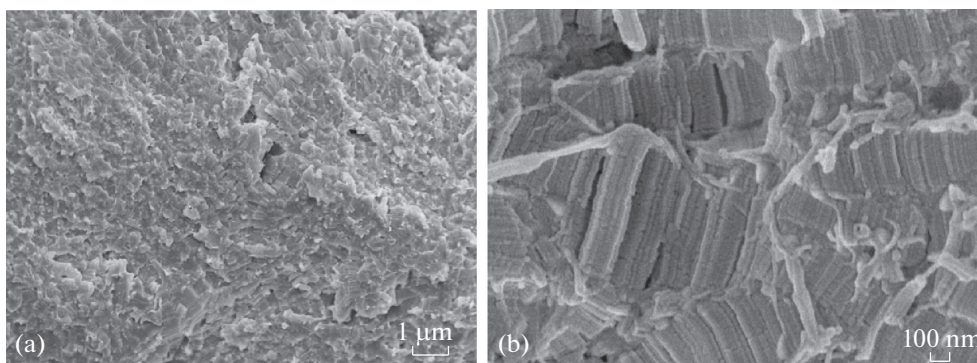


Fig. 1. Image of the cleaved surface of the initial, unfilled PTFE before radiation modification at different magnifications: (a) $\times 6000$ and (b) $\times 100000$.

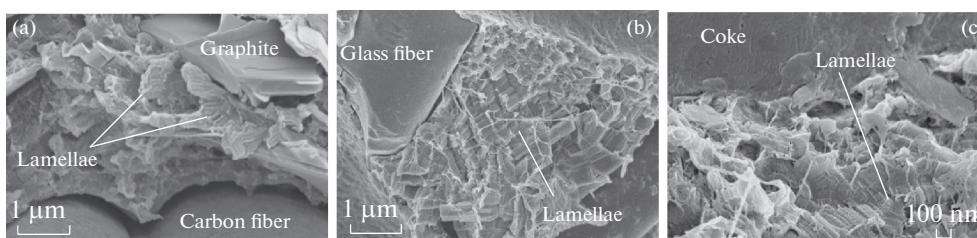


Fig. 2. Images of the surface of cleavages of the typical PTFE composites before radiation modification: (a) F4F15G10, (b) F4S15, and (c) F4K20.

of steel grade 45 with a roughness of $R_a = 0.3$ and a hardness of $HR_c = 45$ was used as a counterbody in accordance with *GOST* (State Standard) 11629-75. The test samples were machined in the form of cylinders with a diameter of 6 mm and a height of 15 mm from rods. The sample was placed at a distance of 25 mm from the disc center. We studied the time dependences of the friction coefficient and the rate of linear wear I_z upon friction:

$$I_z = \frac{\Delta Z}{L},$$

where $L = vt$ is the friction path, v is the linear sliding rate, t is the test duration, ΔZ is a change in the sample's linear size. The values of the friction coefficient and ΔZ were recorded automatically by the tribometer and displayed on the screen in graphical form.

The morphology of the wear products and the friction surfaces of the counterbody and the samples was further investigated using electron microscopy.

RESULTS AND DISCUSSION

Supramolecular structure of the composites. Typical images of the cleavage surface of the initial PTFE without fillers are presented in Fig. 1, reflecting its microscale (Fig. 1a) and nanoscale (Fig. 1b) structures. The supramolecular structure of PTFE is characterized by the formation of lamellae 0.3–1 μm thick

and up to several micrometers in length. The lamellae consist of fibrils oriented perpendicular to the planes of large lamellae. It is seen from Fig. 1b that the fibrils have a substructure, which is a sequence of beads separated by sharp electronic contrast. The typical grain size of the substructure is 15–20 nm.

The introduction of both fibrous and disperse fillers does not lead to a qualitative change in the morphology of the polymer matrix. In all cases, it is characterized by the existence of lamellae. It is seen that large (Figs. 2a and 2b) and small (Fig. 2c) filler particles are surrounded by polymer lamellae that are not different from the lamellae in the initial unfilled PTFE.

The introduction of filler particles, irrespective of their nature and concentration, has little effect on the characteristics of the phase transitions in the polymer, that is, the temperature and enthalpy of melting and crystallization (Table 2). A decrease in the PTFE melting enthalpy to 4 J/g in composites compared to the unfilled polymer corresponds to a decrease in the PTFE crystallinity by approximately 5%.

In unexposed composites, low adhesion between the matrix and particles of organic and inorganic fillers is observed (Figs. 2a, 2b, and 3). It is manifested in the electronic images as the delamination of filler particles and a polymer matrix with the appearance of an interfacial gap. This facilitates an increase in the porosity of the composite compared to the initial,

Table 2. Characteristics of the phase transition of PTFE and PTFE-based composites before radiation modification

Sample	T_m , °C	T_c , °C	ΔH_c , J/g
PTFE	328.5	317.2	25.5
F4KS2	328.1	318.4	21.1
F4S15	328.3	317.5	24.6
F4K20	328.4	316.6	24.1
F4UV15G10	328.1	316.8	22.1
F4Br40G10	327.7	317.1	24.5
F4Br40M10	327.9	316.8	25.0

T_m is the melting point, T_c is the crystallization temperature, and ΔH_c is the crystallization enthalpy.

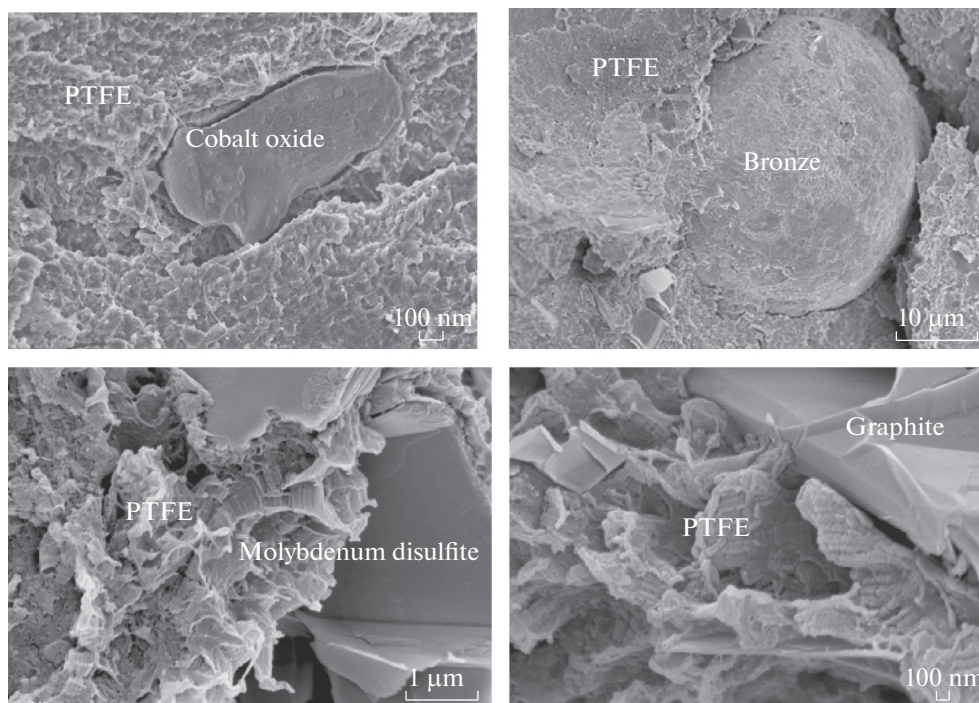
unfilled polymer matrix due to the formation of voids along the edge of the particles. All the fillers used have a higher surface energy compared to PTFE, which leads to their incompatibility and weak interfacial interactions with polymer chains.

Radiation exposure of the composites above the melting point of the polymer matrix leads to radical changes. The first significant difference is that, in all the studied composites after their irradiation in melt with subsequent crystallization, a lamellar structure is not formed (Fig. 4). This fact was previously established for unfilled PTFE [9–11]. On cleavages of the radiation-modified composites, centrally symmetric spherulitic structures (axiolites) with radially directed

fibrils (Figs. 4 and 5) are observed instead of lamellae. The size of these structures is substantially higher than the size of lamellae and varies from 20 to 50 μm , depending on the filler. It is revealed by XMA that filler particles are located in the center of axiolites; that is, filler particles serve as structure-formation centers during crystallization. This process stimulates the emergence of a phase with smaller crystallites: thermograms show the multiplicity of phase transitions (Fig. 6).

Another significant difference is the disappearance of the interfacial separation, namely, the separation of filler particles from the polymer matrix (Figs. 4 and 5). The observed changes clearly indicate that macromolecules are grafted by radiation to the surface of the filler particles. The chemical bonding of PTFE with the filler particles can occur by the direct recombination of macroradicals at the interface or because of the grafting of low-molecular-weight products of radiolysis to the surface and subsequent crosslinking reactions with macromolecules. A distinctive feature of the occurring interfacial processes is the lack of selectivity with respect to the nature of the filler, which is explained by the rather high oxidizing ability of PTFE radiolysis products.

Tribological properties. Changes in the supramolecular structure and interfacial interactions in PTFE composites lead to unprecedented large changes in their tribological properties. Data on the friction and wear of the initial and radiation-modified PTFE com-

**Fig. 3.** Images of the cleavage surface of typical PTFE composites before radiation modification, showing the interfacial separation of filler particles from the polymer matrix: (a) F4KS2, (b) F4Br40, (c) F4Br40M10, and (d) F4Br40G10.

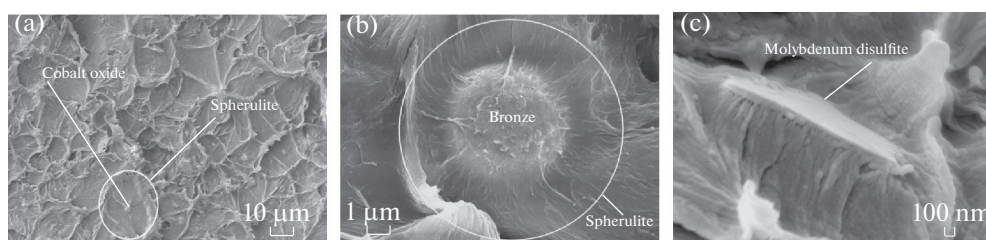


Fig. 4. Images of the cleavage surface of typical PTFE composites after exposure to radiation in the melt (at a dose of 200 kGy), indicating the formation of spherulitic microstructures with the radial orientation of fibrils and centrally symmetric arrangement of the filler particles: (a) F4KS2, (b) F4Br40, and (c) F4Br40M10.

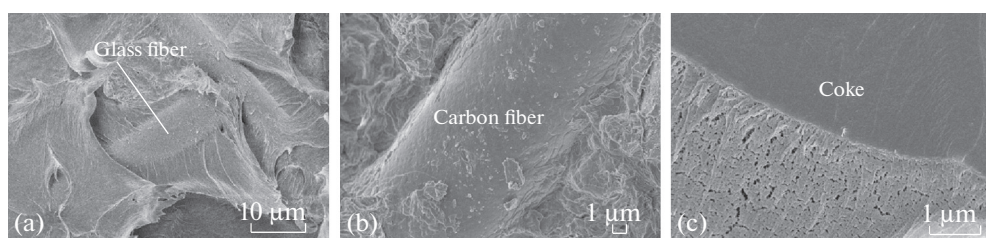


Fig. 5. Images of the cleavage surface of typical PTFE composites after exposure to radiation in the melt (at a dose of 200 kGy), indicating a sharp increase in the adhesive interaction between filler particles and the polymer matrix and the absence of phase separation: (a) F4S15, (b) F4UV15, and (c) F4K20.

posites at a contact pressure of 5 MPa and a sliding rate of 1 m/s without lubrication are given in Tables 3 and 4. Unfilled and unirradiated PTFE is characterized by a very high wear rate, measured by several millimeters per kilometer of friction path. The wear of unfilled PTFE is accompanied by the delamination of large fragments (about 1 mm) of the surface, which are the wear products (Fig. 7). This character of wear of the friction surface is called delamination [12] and is caused by the process of the nucleation and growth of cracks in the sample along the sliding direction at a depth close to the thickness of the wear products. The addition of fillers reduces wear by up to 10^3 times, and the size of wear products decreases by 10–20 times; however, the shape of wear particles changes little (Fig. 8a). It is assumed that the wear reducing mechanism in PTFE composites is associated with partial blocking of the crack growth process with filler particles [12, 13].

Radiation modification in the melt leads to a further decrease in wear. For unfilled PTFE at a dose of 200 kGy, wear decreases by four orders of magnitude and becomes approximately an order of magnitude less than the unirradiated composites, and the wear of irradiated composites decreases up to 50 times with respect to wear before irradiation (Table 4). According to [10, 14], an abnormally high decrease in the wear of unfilled PTFE irradiated in the melt is because of the transition from the delamination to abrasive wear mechanism related to a global change in the supramolecular structure of the polymer. In the composites, additional factors which increase the wear resistance

are enhanced interfacial interaction of the filler particles to the polymer matrix and some features of structure formation: filler particles are firmly anchored in the center of axiolites, from which fibrils radiated.

Signs of the abrasive mechanism of wear for the irradiated PTFE composites are a sharp decrease in the size of wear products (100-fold) with respect to the initial composites, a change in their shape and number

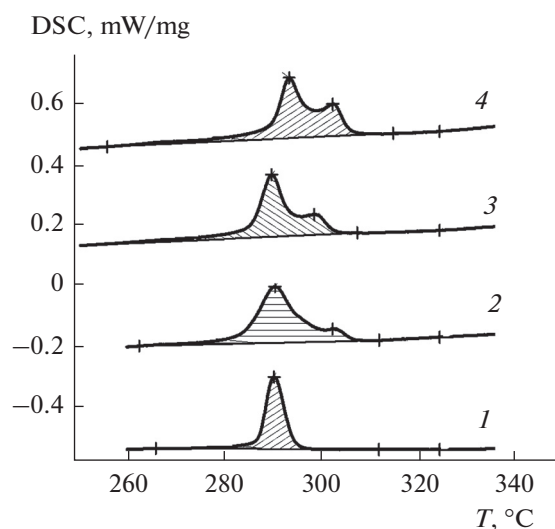


Fig. 6. Crystallization thermograms after radiation exposure in the melt (at a dose of 200 kGy) of (1) F4UV15 PTFE, (2) F4Br40Sav5, (3) F4UV20G10, and (4) F4UV15.

Table 3. Tribological characteristics of PTFE composites before irradiation in the area of steady friction

No.	Sample	Friction coefficient	Temperature in the contact area, °C	Linear wear, µm/km
1	PTFE	0.24	30	4100
2	F4UV15	0.26	60	2.5
3	F4UV15G10	0.17	52	3.4
4	AFG80VS	0.23	65	7.2
5	F4S15	0.28	67	3.5
6	F4Br40G5	0.16	45	3.9
7	F4Br40M10	0.22	55	5.2

Table 4. Tribological characteristics of PTFE composites after exposure to radiation (at a dose of 200 kGy) above the melting point of the crystallites in the area of steady friction

No.	Sample	Friction coefficient	Temperature in the contact area, °C	Linear wear, µm/km
1	PTFE	0.18	50	0.3
2	F4K20	0.21	55	0.1
3	AFG80BS	0.22	55	0.2
4	F4UV15	0.18	50	0.1
5	F4UV15G5	0.18	47	0.1
6	F4UV15G10	0.15	40	0.2
7	F4UV15M5	0.14	50	0.1
8	F4UV15M10	0.14	47	1.0
9	F4S15	0.26	60	0.5
10	F4Br40	0.18	47	<0.1
11	F4Br40G5	0.19	46	<0.1
12	F4Br40M2	0.21	53	0.1
13	F4Br40M10	0.24	51	1.3
14	F4Br60	0.18	50	0.5

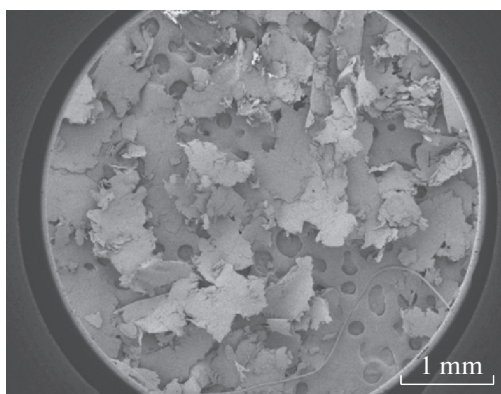
(Fig. 8b), the islet nature of the polymer transfer film formed as a result of friction at the counterbody, and the existence of many grooves and scratches on the

friction surface of the irradiated sample and their absence on the surface of the initial polymer (Fig. 9).

CONCLUSIONS

The supramolecular structure of PTFE composites prior to radiation modification is characterized by the existence of fibrillar lamellae in the polymer matrix and the interfacial separation of polymer and filler particles. The characteristics of phase transitions in a polymer matrix, i.e., the temperature and enthalpy of melting and crystallization and the crystallinity, does not depend on the nature and concentration of the filler.

Radiation modification in the melt leads to a significant change in the supramolecular structure, the characteristics of phase transitions, and the properties of the composites. The supramolecular structure of the irradiated composites is characterized by the disappearance of a phase separation and the formation of

**Fig. 7.** Wear products for the initial PTFE.

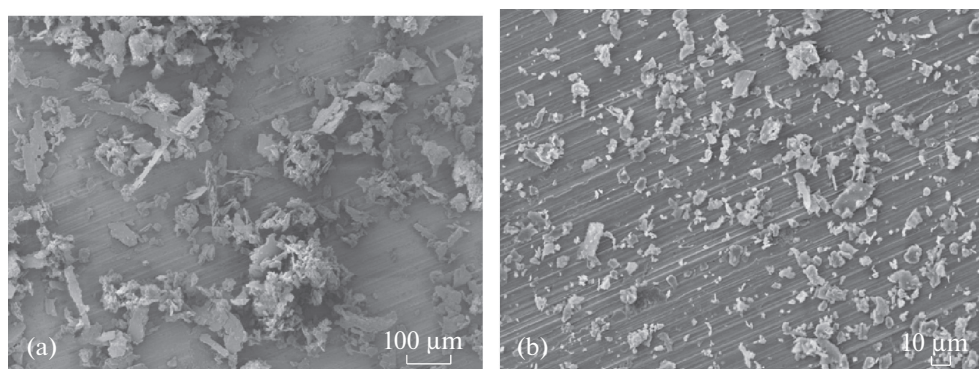


Fig. 8. Wear products of the composite F4Br40G10: (a) initial composite and (b) after exposure to radiation in the melt (at a dose of 200 kGy).

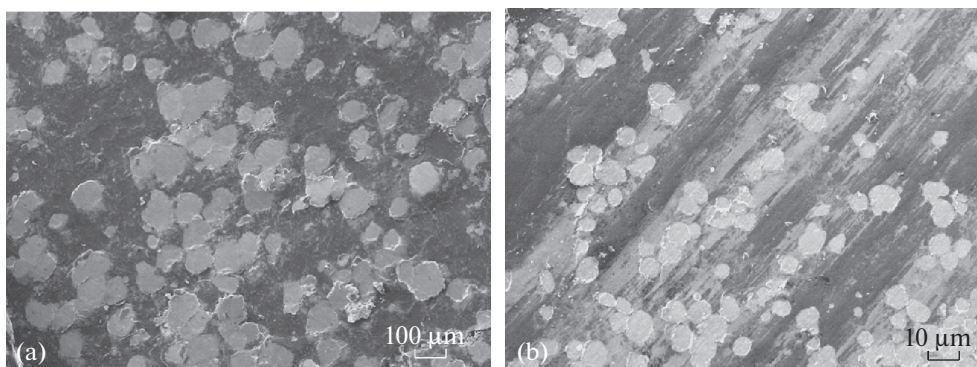


Fig. 9. Images of the friction surface of the composite F4Br40Sav5: (a) initial composite and (b) after exposure to radiation in the melt (at a dose of 200 kGy).

axiolites with the radial orientation of fibrils, in the center of which the filler particles are located. Changes in the structure are explained by an increase in interfacial interactions through the radiation grafting of macromolecules (and low-molecular-weight products) to the surface of the filler particles. The transition from the lamellar to centrally symmetric radial packing of fibril leads to the emergence of a phase with the smallest crystallites and a change in the phase-transition characteristics, that is, the appearance of multiplicity and lowering of the melting and crystallization temperature.

Irradiation under specified conditions results in a drastic improvement in the tribological properties of the composites. The linear wear rate of the irradiated composites is 50 times lower relative to the unirradiated samples. The correlation of the wear value or the friction coefficients, associated with the nature of the filler, is manifested rather weakly, which is in agreement with the HRSEM data. The supramolecular structure of the irradiated composites promotes the full blocking of the delamination wear mechanism inherent in the initial PTFE and its unirradiated com-

posites and the transition to the abrasive wear mechanism.

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REFERENCES

1. N. P. Istomin and A. P. Semenov, *Antifriction Properties of Composite Materials Based on Fluoropolymers* (Nauka, Moscow, 1984) [in Russian].
2. B. A. Loginov, A. L. Villemson, and V. M. Buznik, *Russian Fluoropolymers: History, Technology, and Prospects* (Moscow, 2013) [in Russian].
3. V. A. Kargin, G. L. Slonimskii, and T. I. Sogolova, in *Polymer Science Problems: Selected Papers* (Nauka, Moscow, 1986) [in Russian].
4. G. H. Michler and F. J. Balta-Calleja, *Mechanical Properties of Polymers Based on Nanostructure and Morphology* (Taylor&Francis, London, 2005).

5. A. A. Okhlopkova, P. N. Petrova, S. N. Popov, and S. A. Sleptsova, *Russ. Khim. Zh.* **52** (3), 147 (2008).
6. M. Conte and A. Igartua, *Wear* **296**, 568 (2012).
7. S. A. Khatipov and N. A. Artamonov, *Russ. Khim. Zh.* **52** (3), 89 (2008).
8. A. V. Petrovskaya and S. A. Khatipov, *Materialovedenie*, No. 4, 49 (2011).
9. S. A. Khatipov, S. A. Serov, N. V. Sadovskaya, and E. M. Konova, *Radiat. Phys. Chem.* **81** (3), 256 (2012).
10. E. M. Konova, *Candidate's Dissertation in Chemistry* (Karpov Res. Phys.-Chem. Inst., Moscow, 2014).
11. S. A. Khatipov, S. A. Serov, N. V. Sadovskaya, and E. M. Konova, *Polymer Sci., Ser.* **54** (9), 684 (2012).
12. T. A. Blanchet and F. E. Kennedy, *Wear* **14**, 229 (1992).
13. K. Tanaka and S. Kawakami, *Wear* **79**, 221 (1982).
14. S. A. Khatipov, S. A. Serov, and N. V. Sadovskaya, *Vopr. Materialoved.* **72** (4), 191 (2012).

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