

Spectroscopic Study of Tribooxidation Processes in Modified PTFE

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Abstract—The effect of layered silicates on the structure and performance characteristics of polytetrafluoroethylene is studied using IR spectroscopy, X-ray photoelectron spectroscopy, and scanning electron microscopy, as well as tribological and physicomechanical testing. It has been shown that the filling of polytetrafluoroethylene with layered silicates leads to a substantial (up to 2500 times) decrease in its mass wear rate, while its strength characteristics remain similar to those of the original polymer. The use of IR spectroscopy and X-ray photoelectron spectroscopy to study structural transformations that occur during the friction of the polymer composite materials with various compositions of fillers has revealed the formation of intermediate products in the course of the oxidative destruction of polytetrafluoroethylene.

Keywords: polytetrafluoroethylene, layered silicate, serpentinite, kaolinite, vermiculite, magnesium spinel, IR spectroscopy, X-ray photoelectron spectroscopy, wear resistance, thermally expanded graphite

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INTRODUCTION

Filling is known to be the most popular method for the structural modification of polytetrafluoroethylene (PTFE), which is carried out to minimize its drawbacks, such as cold flow, low wear resistance, and a high coefficient of linear thermal expansion, which restricts its use in important friction units [1]. One of the most advanced approaches to modifying the a polymer matrix is to fill it with layered silicates, which are abundant and well known as clay minerals. Heightened interest in layered silicates as modifiers of polymers can be explained by their ability of dispersing to form nanosized particles, which makes it possible to produce intercalated and exfoliated composites with enhanced properties compared to those of the matrix polymer. In developing tribological materials, interest in layered silicates is due to the possibility of creating self-lubricating polymer nanocomposites. An attractive fact is also that, when even a small amount (2–3 wt %) of clay is added to a polymer matrix, its coefficient of thermal expansion decreases substantially [2, 3].

The known polymer nanocomposites based on nonpolar or weakly polar polymers filled with layered silicates do not possess high performance characteristics like materials based on polar polymers [4, 5]. The data on the effect of these fillers on the properties of PTFE-based composites are nearly lacking. This can be explained primarily by the hydrophilic behavior of the silicates, which is one of the key factors of their incompatibility with organic polymer matrices. In order to eliminate this difficulty, the silicates are treated by surfactants, modified by functional addi-

tives, and subjected to mechanical activation, as well as use other methods of surface modification [6].

Tribochemical reactions of macromolecules that occur during the friction of polymer composites play a significant role in developing methods for enhancing their wear resistance and understanding mechanisms of their friction. Although considerable efforts are being made in studies in this field, no clear concept of mechanisms and elementary stages of the tribochemical reactions have been developed. This can be explained by both the poor accessibility of the zone of contact for examination and a large number of possible mechanisms of the initiation of chemical processes in polymers by triboactivation. It is known that friction, which is the process of the interaction of two rubbing surfaces, is accompanied by the deformation, heating, and cooling of these surfaces, as well as changes in the composition of surface layers that occur under the effect of environment, diffusion, and transfer phenomena [7]. In the course of friction, repeated elastic deformations reduce the strength of macromolecules, and the most heavily loaded bonds are ruptured due to mechanical stresses [8] to form low-molecular products, which contain end radicals. It is of interest to study processes that accompany the friction of modified PTFE since they govern the tribological behavior of friction pairs with the members made of this material.

The aim of this work was to carry out a structural study of tribological processes that occurred in PTFE modified by layered silicates.

Table 1. Physicomechanical and tribological characteristics of PCMs containing layered silicates

Composite	Elongation at rupture, %	Ultimate tensile strength, MPa	Mass wear rate I , 10^{-6} kg/h	Coefficient of friction f
PTFE	300–320	20 ± 2	70–75	0.04–0.2
PCM containing mechanoactivated layered silicates				
PTFE + 2 wt % serpentinite (S)	315	21	0.20	0.02
PTFE + 5 wt % S	270	18	0.07	0.02
PTFE + 7 wt % S	245	17	0.05	0.03
PTFE + 2 wt % vermiculite (V)	328	17	5.30	0.02
PTFE + 5 wt % V	130	11	1.80	0.02
PTFE + 10 wt % V	75	11	1.30	0.02
PCM containing mechanoactivated layered silicates and magnesium spinel				
PTFE + 1.0 wt % S + 1.0 wt % NMS	355	24	0.13	0.03
PTFE + 1.5 wt % S + 0.5 wt % NMS	315	22	1.07	0.03
PTFE + 1.8 wt % S + 0.2 wt % NMS	330	21	2.23	0.04
PTFE + 4.0 wt % S + 1.0 wt % NMS	320	20	0.03	0.04
PTFE + 4.5 wt % S + 0.5 wt % NMS	345	21	0.03	0.03
PTFE + 4.8 wt % S + 0.2 wt % NMS	335	19	0.27	0.03
PTFE + 1.8 wt % V + 0.2 wt % NMS	360	19	2.53	0.04
PTFE + 1.5 wt % V + 0.5 wt % NMS	318	17	4.00	0.03
PTFE + 1.0 wt % V + 1.0 wt % NMS	325	15	4.33	0.03
PTFE + 4.8 wt % V + 0.2 wt % NMS	302	15	2.03	0.03
PTFE + 4.5 wt % V + 0.5 wt % NMS	290	15	0.70	0.04
PTFE + 4.0 wt % V + 1.0 wt % NMS	243	13	3.40	0.04
PTFE + 6.8 wt % V + 0.2 wt % NMS	322	13	0.03	0.03
PTFE + 6.5 wt % V + 0.5 wt % NMS	323	14	0.13	0.04
PTFE + 6.0 wt % V + 1.0 wt % NMS	358	11	0.13	0.03

EXPERIMENTAL

The objects of the study were polymer composite materials based on grade-PN PTFE (GOST 10007–80). The polymer was filled with natural layered silicates, such as serpentinite (the Kovdor deposit, Murmansk Region, Russia) and vermiculite (the Inaglinskoe deposit, Republic of Sakha (Yakutia), Russia); nano-sized magnesium spinel (NMS) with an average particle size of 70 nm, which was synthesized at the Institute of Solid State Chemistry and Mechanochemistry of the Siberian Branch of the Russian Academy of Sciences (Novosibirsk) using the mechanochemical method, was used as a functional additive. The magnesium spinel had the chemical formula $MgO \cdot Al_2O_3$.

The preparation of PTFE included its drying for 4 h at a temperature of 180°C. Dried PTFE was milled and bolted through sieve no. 1K. Vermiculite was dried in a furnace for 10 min at a temperature of 900°C in order to disintegrate silicate plates into individual layers via the thermal expansion of vermiculite (swelling, which was typical of vermiculite), which resulted from the removal of crystallization water contained in this

mineral. Serpentinite was dried in a furnace for 4 h at a temperature of 120°C in order to remove surface-bound moisture [9]. The dried silicates were activated using an AGO-2 planetary-type mill for 2 min at a rotational velocity of the drums of 3000 rpm. The composites were produced by the dry mixing of the polymer with the filler using a blade mixer followed by the free sintering of the mixture.

The physicomechanical characteristics of the polymer materials were measured in accordance with GOST 11262–80 using an Autograph AGS-J testing machine (Shimadzu, Japan). The tribological characteristics were determined in accordance with GOST 11629–75 using the shaft–bushing test arrangement implemented in an SMTs-2 friction machine (Russia) under a load of 0.45 MPa at a velocity of sliding of 0.39 m/s. Specimens were shaped as bushings 32–22 mm in diameter with heights of 21 mm; the counterbody was a steel shaft with a hardness of 45–50 HRC and a surface roughness of 0.06–0.07 μm . The results of the tests are presented in Table 1. The duration of the tests was 3 h.

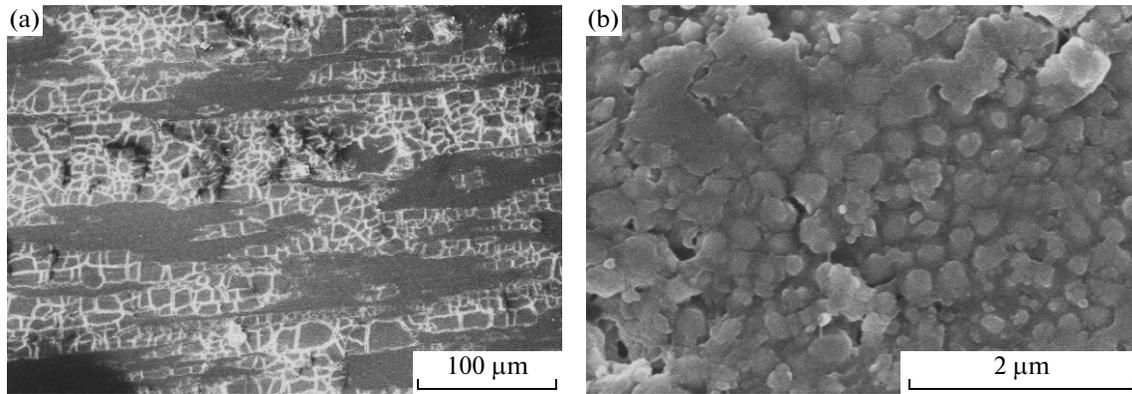


Fig. 1. Micrographs of friction surfaces of composites containing (a) 2 wt % of serpentine and (b) 2 wt % of serpentine + 0.5 wt % of NMS.

Structural examinations of the friction surfaces were carried out using scanning electron microscopy, IR spectroscopy, and X-ray photoelectron spectroscopy (XPS). The friction surfaces of the composites were examined using a JSM-7800F scanning electron microscope (Jeol Ltd., Japan) equipped with an energy dispersive attachment. Structureless conductive films were produced on the surfaces using the plasma deposition of platinum, which provided the highest secondary-electron yield. IR spectra were recorded using a FTIR 7000 spectrometer (Varian Inc., United States); the spectra were identified and analyzed in the $550\text{--}4000\text{ cm}^{-1}$ frequency range using the known methods, the spectrometer library, and the data on IR spectra of polymers. XPS spectra were recorded using a K-Alpha spectrometer (Thermo Scientific, the USA) in AlK_{α} radiation at a power of 100 W and a voltage of 12 kV. The zone of analysis was $30\text{--}400\text{ }\mu\text{m}$ in diameter.

RESULTS AND DISCUSSION

Table 1 presents the results of the physicomechanical and tribological tests of the polymer composite materials (PCMs) based on PTFE and the layered silicates. The concentration of the filler in the composites varies from 2 to 7 wt %; in the composites containing vermiculite, the concentration of the filler is 10 wt %.

It can be seen from the data given in Table 1 that the introduction of layered silicates into PTFE favors the retention of the mechanical characteristics of the material, while its mass wear rate and coefficient of friction substantially decrease. Unlike the known antifriction polymer materials that contain traditional fillers, the composites that contain layered silicates have both high wear resistance and high mechanical characteristics. A promising trend is to combine layer silicates with functional additives, such as NMS. This enhances the wear resistance of the composites by up to 2500 times. The prerequisite for using NMS as a functional additive is the capabil-

ity of their nanoparticles of becoming self-organized; due to their extremely high activity, the nanoparticles tend to form clusters in the bulk of the material, which favors the reinforcement of the material and the enhancement of its strength characteristics [10].

One of the causes of the substantial decrease in the mass wear rate may be structural transformations in the surface layer of the material, which result from the tribochemical reactions occurring in the course of friction. Some authors believe that the mechanical, physical, and chemical interactions of the surfaces in contact, as well as the disintegration and recombination of molecules and structural transformations, which occur under the effect of friction, result in the formation of a new structure similar to the structure of thermotropic liquid crystals, which provides the easy sliding of sublayers and enhances the wear resistance of the surface layer [11–13]. In this case, friction is accompanied by the formation of zones that consist of particles of filler transferred from the boundary zones of various supramolecular structures on the friction surface. Micrographs of friction surfaces of composites clearly show zones that consist of silicate particles (Fig. 1). Due to their layered structure, these surface silicate structures apparently play the role of a lubricant, which favors the creation of conditions for boundary friction. This can also explain the very low coefficient of friction of composites that contain serpentine and vermiculite.

In order to evaluate the effect of the fillers on the friction and wear of the composites, their surfaces were examined using IR spectroscopy and XPS. Figure 2 shows the IR spectra of specimens of composites recorded before and after friction.

The IR spectrum of original PTFE contains the intense absorption bands; these bands correspond to the valent oscillations of the $-\text{CF}_2-$ group at 1211 and 1154 cm^{-1} and the ν oscillation (CC), which appears as the inflection at 1233 cm^{-1} , as well as the deformation and out-of-plane oscillations of $-\text{CF}_2-$ groups,

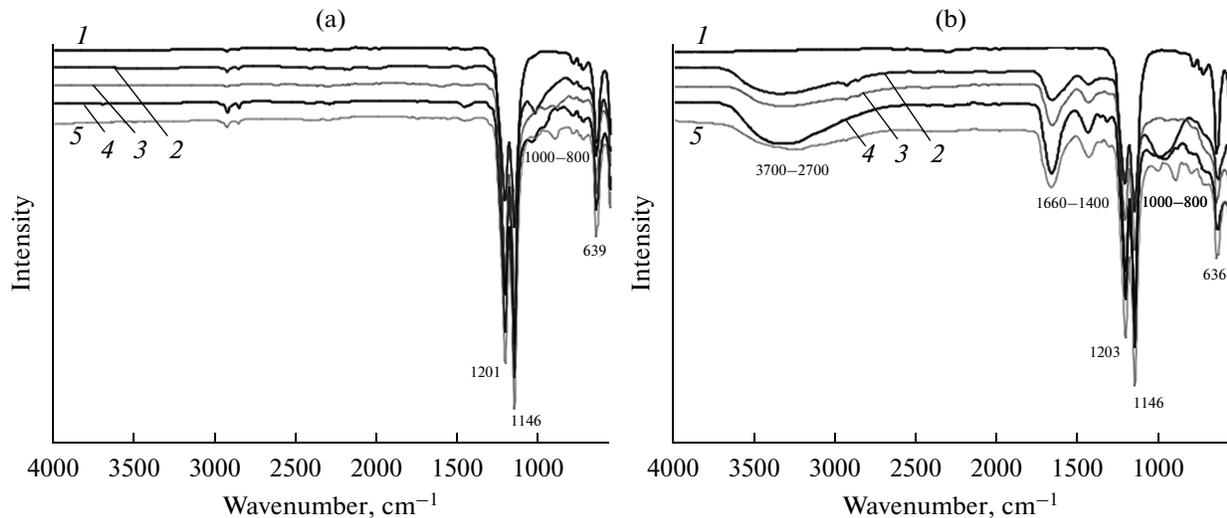


Fig. 2. IR spectra of specimens of PCMs recorded (a) before and (b) after friction: (1) PTFE; (2) PTFE + 2 wt % of vermiculite; (3) PTFE + 2 wt % of vermiculite + 0.5 wt % of NMS; (4) PTFE + 2 wt % of serpentinite; and (5) PTFE + 2 wt % of serpentinite + 0.5 wt % of NMS.

i.e., the wagging oscillations $\gamma\omega$ ($-\text{CF}_2-$) at 639 cm^{-1} . It is known that the physical state of the friction surface of a solid is characterized by the presence of surface films of a definite composition and specific features of the structure of the surface layers [14]. Under real conditions in air, all microasperities and microcracks on the surface become covered with oxide films, as well as layers of adsorbed molecules of gases and water, nearly instantaneously, i.e., within a period of a few hundredths to a few thousandths of a second. These films certainly influence the processes of friction, which involve the severe deformation and the inevitable fracture of the rubbing surfaces. The IR spectra of the composites modified by metal-containing fillers, which have been recorded after friction in the range of $3600\text{--}2600\text{ cm}^{-1}$, contain a wide absorption band. It is known that the appearance of narrow absorption bands in this range is typical of free, nonassociated hydroxyl groups of alcohols. In accordance with the data from [15], the appearance of a wide absorption band in the ranges that are typical of the oscillation of the bond in the $\text{OH}-$ group is due to the formation of associates of the hydrogen bond; moreover, peroxides have been identified in this range. The IR spectra of the peroxides contain the characteristic bands at $830\text{--}890\text{ cm}^{-1}$, which correspond to the valence oscillations of the $-\text{O}-\text{O}-$ group (weak absorption), and $3545\text{--}3562\text{ cm}^{-1}$, which correspond to the valence oscillations of $\text{HO}-$ in the free $\text{HOO}-$ group. This means that, in both cases, the presence of these bands in the spectra is indicative of the formation of an intermediate product of the oxidation of the carbon chain. The appearance of these oxygen-containing groups serves as evidence of the participation of peroxide radicals in the destruction reactions; it is

highly likely that these radicals result from the reactions of low-molecular products of the initial destruction of the polymer chain in the form of radical particles with oxygen, which is consumed for these reactions from atmospheric air and oxide films [8]. Among numerous intermediate products, compounds that contain ethylenic bonds and carbonyl groups can be formed. The further oxidation of these products inevitably leads to the formation of carboxylates with the participation of cations of the metals contained in the fillers or the counterbody material. This is confirmed by the presence of two characteristic peaks in the range of $1680\text{--}1400\text{ cm}^{-1}$ in the IR spectra of all composites modified by the metal-containing fillers. It is noted in [15] that carboxylates, which have the ionic structure, are characterized by the presence of two intense absorption bands at $1680\text{--}1610$ and $1400\text{--}1300\text{ cm}^{-1}$ in the IR spectra; these bands correspond to the asymmetric and symmetric oscillations of the two equivalent $\text{C}=\text{O}$ bonds. We note that the IR spectra of the composites modified by the fillers that contain no metal (the composites containing thermally expanded graphite (TEG), Fig. 3) are also characterized by the presence of the bands typical of carboxylates in the above-mentioned frequency ranges. The energy dispersive analysis of the friction surfaces of the composites containing TEG has revealed the presence of iron and oxygen ions, which can be indicative of the participation of iron ions contained in the counterbody material in the formation of carboxylates (Fig. 4). The wear resistance of composites modified by TEG is fairly low. This can serve as evidence against a significant role of the metals contained in the filler in the processes of structure formation, such as cross-linking

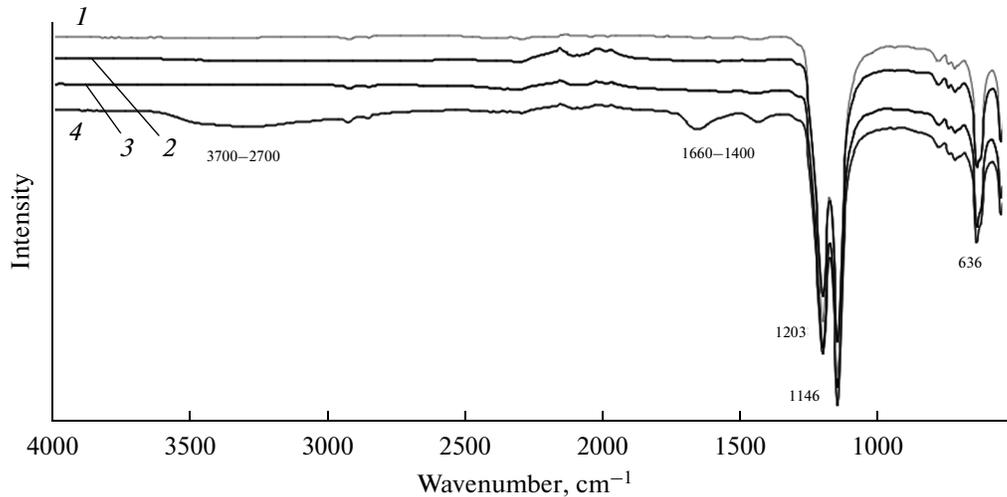


Fig. 3. IR spectra of specimens of PCMs: (1) PTFE + 2 wt % of TEG, recorded before friction (2 MPa, 0.25 m/s); (2) PTFE + 2 wt % of TEG, recorded after friction (2 MPa, 0.25 m/s); (3) PTFE + 2 wt % of TEG, recorded before friction (0.45 MPa, 0.39 m/s); and (4) PTFE + 2 wt % of TEG, recorded after friction (0.45 MPa, 0.39 m/s).

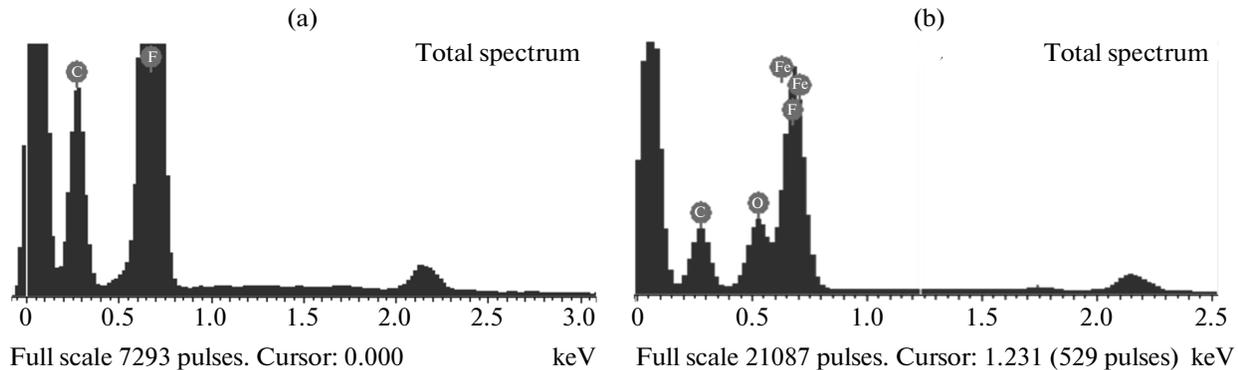


Fig. 4. Results of elemental analysis of specimens of PTFE + 2 wt % of TEG composite subjected to friction under different conditions: (a) 2 MPa, 0.25 m/s and (b) 0.45 MPa, 0.39 m/s.

and possibly the modification of the matrix, which occur along with the processes of destruction.

It is possible that the formation of carboxylates favors the inhibition of the oxidation processes since carboxylic acids are the end product of oxidation. The probability of the simultaneous occurrence of the processes of structure formation and the processes of the destruction of polymer macromolecules is high because the radical particles, which can appear in a large amount and variety under the effect of a number of factors acting during friction, such as homolysis, thermolysis, reactions of peroxides with metal cations, etc., will react with each other to form a new bond or, in this case, a cross link (in organic chemistry, this stage is the final stage of radical processes).

The results of IR spectroscopy are confirmed by the XPS data. Figure 5 shows the high-resolution XPS spectra of the lines F1s and C1s recorded for the PTFE specimen and the specimens of the composites based

on PTFE and serpentinite. For the specimen of the original polymer, the position and shape of the lines F1s (688.33 eV) and C1s (291.77 eV) correspond to $\text{CF}_2\text{-CF}_2$ groups [16]. The ratio of the number of fluorine atoms to the number of carbon atoms (F : C) in the original PTFE is ~ 2 , which also correlates well with the structure of the fragment ($-\text{CF}_2\text{-CF}_2-$). In the original PTFE, no oxygen has been identified, which corresponds to the high chemical inertness of this polymer; however, the concentration of oxygen in the specimens subjected to friction is 2.65% (the line O1s with the energy of 531.36 eV). After friction, the ratio F : C decreases to 1.24 for the original PTFE and to 0.33 for the composite. This is indicative of the defluorination of the surfaces of the composite and PTFE due to the thermal-oxidative destruction of the polymer accompanied by the rupture of the C–F bond, which may lead to the formation of fluorides, in particular on the counterface. This assumption has

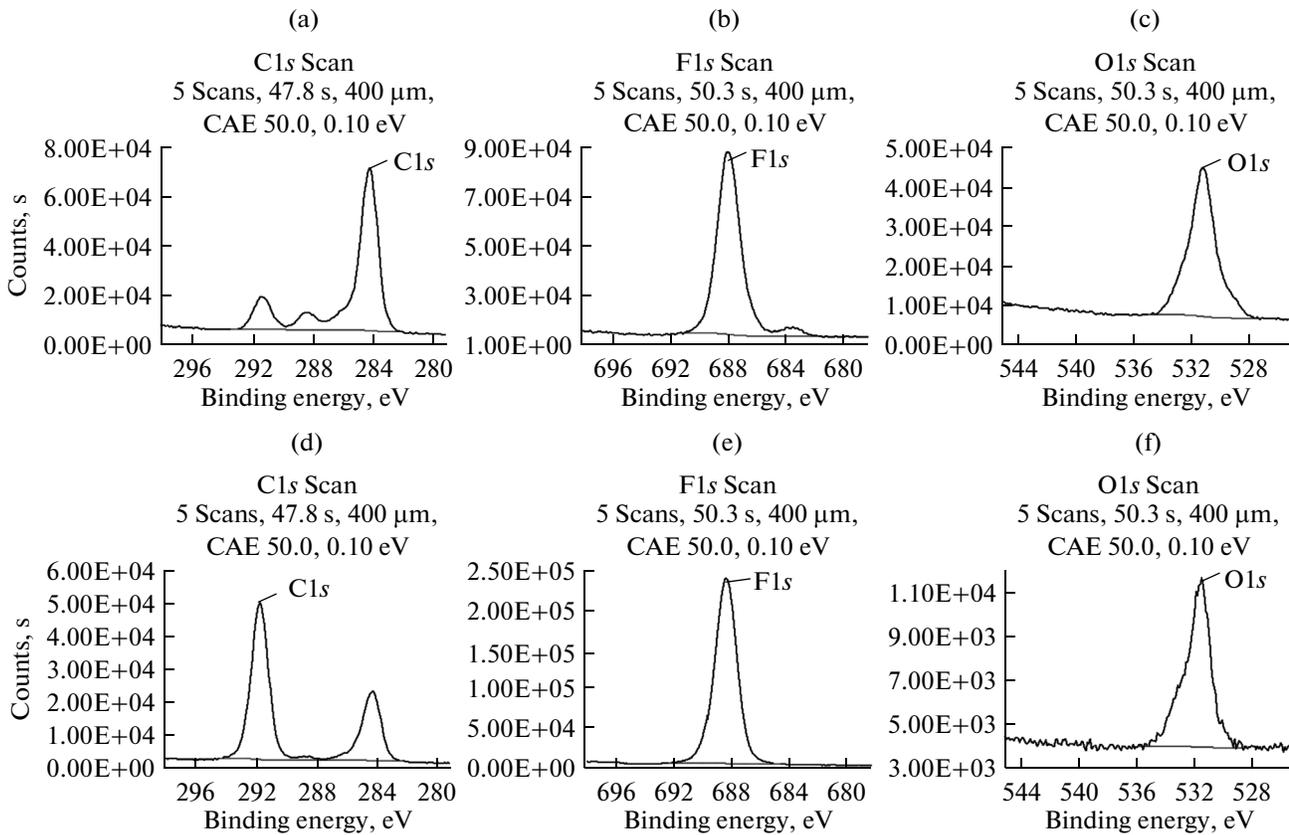


Fig. 5. XPS spectra of specimens of (a)–(c) PTFE + 2 wt % of serpentinite composite and (d)–(f) PTFE subjected to friction: (a) C1s; (b) F1s; (c) O1s; (d) C1s; (e) F1s; and (f) O1s.

been confirmed in work [17] in which possible mechanisms of the chemical reactions that occur during the friction of PTFE against a metal counterbody are studied. In this work, metal fluorides have been identified on the counterface using XPS.

After the friction of the original PTFE, the position of the line F1s remains unchanged, but the subsidiary peak with the binding energy of 284.28 eV appears for the line C1s. This peak has a high probability of corresponding to the energy of the C=O bond, which is equal to 284.3 eV ([18, 19]).

After the friction of the composites, the position of the line F1s remains nearly unchanged; however, for the line C1s the widening of the spectrum toward

lower binding energies is observed, which is indicative of the superposition of a few lines that correspond to different chemical states. The approximation of the spectrum has revealed the subsidiary peaks with binding energies of 284.56 and 288.48 eV, which can be attributed to C–C (284.5 eV) and O–C=O (288.4 eV) bonds, respectively [20]. This is also indicative of the destruction of the polymer, the depletion of the surface of fluorine and, hence, the formation of C–C bonds and a carboxylate group. After friction, the concentration of oxygen in the specimens sharply rises and reaches the value of 16.11%, which confirms the occurrence of the destruction of the polymer during friction in the oxygen-containing environment.

Table 2. Elemental composition of specimens of PTFE and composites on its basis

Specimen	Elemental composition, %			
	C	F	O	F : C
PTFE	33.5	66.5	–	1.99
PTFE subjected to friction	43.34	54	2.65	1.24
PTFE + 2 wt % serpentinite subjected to friction	62.98	20.91	16.11	0.33

CONCLUSIONS

The spectroscopic study of the friction surfaces of the composites has shown that the complex tribological processes, which occur on these surfaces under friction, are accompanied by the oxidation processes the severity and depth of which apparently depend on the origin and the structural activity of the modifiers and which result in the formation of intermediate and end oxidation products; the formation of peroxide radicals; and the destruction of the polymer followed by the rupture of both C–C and C–F bonds.

The obtained results allow us to assume that the key role in the wear resistance of the polymer composites based on PTFE is played by the origin of the metal contained in the fillers; this metal not only influences the character of the oxidation processes, which occur in accordance with the radical mechanism, but can also primarily affect the processes of structure formation.

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