

Effect of Organomodified Layered Silicates on the Properties and Structure of Polytetrafluoroethylene

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Abstract—The physicomechanical and triboengineering properties and the structures of polymer composite materials based on polytetrafluoroethylene and layered silicates are studied. The triboengineering characteristics are substantially improved by the introduction of a small amount of layered silicates (2–5 wt %). It is found that the introduction of organomodified layered silicates leads to a considerable reduction in the friction coefficient, by an order of magnitude, and causes an increase in wear resistance (2000-fold). With the use of X-ray structural analysis and scanning electron microscopy, it is shown that, during friction loading, filler particles are localized on the friction surface, thereby hampering wear of the material.

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INTRODUCTION

One of the promising trends in modern materials science involves the development of polymer composite materials for triboengineering purposes with high performance characteristics. Effective methods for creating these materials include the application of polymer matrixes that a priori feature special characteristics. Owing to a complex of unique physicomechanical, chemical, and triboengineering properties, polytetrafluoroethylene (PTFE) is the most suitable for the manufacture of parts of machine friction units. PTFE displays exceptional frost resistance, high chemical resistance and thermal stability, and a low friction coefficient [1]. PTFE has, along with these advantages, such disadvantages as low wear resistance and high creep, which restrict its application at high specific loads and sliding velocities typical for operational conditions in friction units of various machines and equipment. The mentioned disadvantages can be eliminated via the introduction of various modifiers into the polymer matrix. The application of nanoscale fillers makes it possible to implement qualitative changes in the characteristics of the material and to substantially improve its performance characteristics. In the present study, these purposes are achieved with the use of layered silicates (vermiculite and bentonite) as fillers for the polymer matrix. A layer of a silicate clay mineral has a thickness of about 1 nm and consists of blades approximately 100 nm in width, thereby comprising a filler with a very high ratio of linear sizes [2].

The properties of initial polymers may be considerably improved in the case of intercalation of polymer

macromolecules into the interlayer space of silicates followed by exfoliation into separate nanolayers [3–5]. The main problem encountered in the production of intercalated or exfoliated structures consists in the incompatibility of silicates with an organic polymer matrix due to its hydrophilicity. To create conditions for clay dispersion in polymers and penetration (intercalation) of macromolecules in spaces between silicate plates, the clay is preliminary modified with various types of surfactants. The surfactants create organophilic layers in the interlayer spaces of the clay, thereby providing a high level of polymer compatibility with the filler. Precisely these properties of organophilic layers determine the ability of the clay to be dispersed in the polymer [6].

The goal of the present study is to compare the tribological and stress–strain properties of polymer composites based on PTFE filled with organomodified bentonite and vermiculite.

EXPERIMENTAL

The composites were prepared via a common technique that includes filler treatment with a surfactant solution, mechanical activation, blending with PTFE powder, pressing of the blend, and sintering of the precursors. The research objects were commercial polytetrafluoroethylene (the trademark PN-90), vermiculite from the Inaglinsk deposit in Sakha (Yakutia), and bentonite from the Khakassia deposit. Alkyldimethylbenzylammonium chloride (ADMBAC, Hutsman) and cetyltrimethylammonium bromide (CTAB) were used as surfactants.

Polytetrafluoroethylene was prepared via drying at 180°C for 4 h. The dried PTFE was ground and sieved. Vermiculite was dried in a furnace at 900°C for 10 min (It is known [7] that the loss of crystallization water occurs in the temperature range 800–900°C.). The dried vermiculite was treated with a 10⁻⁶ mol/L solution of ADMBAC for 24 h. Then, vermiculite was activated in an AGO-2 planetary-type mill for 2 min [8]. Bentonite was prepared as follows: It was first dried for 6 h at 120°C [3], and then a solution of CTAB in distilled water (a concentration of 10⁻⁶ mol/L) was prepared. The adsorption of the surfactant on aluminosilicate was conducted for 24 h. The resulting bentonite was filtered off and dried for 24 h. The dried bentonite was subjected to mechanical activation in the AGO-2 planetary-type mill for 2 min.

The composites were obtained via dry blending of the polymer with the filler in an SL-1500 blade-type blender (Russia) at a rotation velocity of 1000 rpm and room temperature for 3 min followed by sintering. The tribological tests were performed on an SMTs-2 friction machine (Russia) according to the roller–bushing friction scheme at a load of 0.45 MPa and a sliding velocity of 0.39 m/s (ASTM D 1894-08). The physico-mechanical properties of the composites were characterized by relative elongation at break ε and ultimate tensile strength σ_u via standard methods (ASTM D 638) with the use of Shimadzu AGS-J testing machines (Japan). The X-ray structural analysis of the composites was performed on an ARL X'TRA diffractometer (Switzerland) using CuK α radiation ($\lambda = 1.5405 \text{ \AA}$) during scanning with a step of 0.04 deg and 3-s accumulation at each point. The friction surfaces and supramolecular structures of polymer composite materials (PCMs) were studied on a JEOL JSM-7800F scanning electron microscope (Japan).

Table 1. Physicomechanical and triboengineering properties of the composites bearing vermiculite

| Vermiculite content, wt % | ε , % | σ_u , MPa | I , mg/h | f |
|----------------------------------|-------------------|------------------|------------|-----------|
| 0 | 351 | 21 | 125 | 0.04–0.20 |
| 2 | 280 | 20 | 6.1 | 0.2 |
| 5 | 238 | 16 | 0.7 | 0.2 |
| 10 | 143 | 11 | 0.07 | 0.18 |
| Vermiculite modified with ADMBAC | | | | |
| 2 | 316 | 22 | 3.66 | 0.02 |
| 5 | 207 | 16 | 0.5 | 0.04 |
| 7 | 183 | 15 | 0.36 | 0.02 |
| 10 | 113 | 14 | 0.16 | 0.03 |

Here and in Table 2, I is the velocity of wear, and f is the coefficient of friction.

RESULTS AND DISCUSSION

Table 1 shows the results of physicomechanical and triboengineering tests of the composites based on PTFE and vermiculite.

The physicomechanical and triboengineering testing of the composites containing vermiculite demonstrates improvement in the characteristics of PCMs bearing surface-modified vermiculite. For example, the strength characteristics of PCMs based on vermiculite modified with ADMBAC are somewhat higher than those of the composite lacking ADMBAC. Moreover, the wear resistance of the composite containing 5 wt % vermiculite modified with ADMBAC increased by a factor of 250 relative to that of the initial PTFE and by a factor of 1.5 relative to that of the composite without ADMBAC. One of the possible factors responsible for the increase in the wear resistance of these materials may be strengthening of the adhesion interaction of composite components due to the effective participation of the filler in the formation of a boundary layer at the polymer/filler interface. Furthermore, it is additionally possible that silicate particles are displaced on the material surface as a result of a friction interaction, a situation that may likewise affect wear resistance.

The physicomechanical and triboengineering properties of the composites containing bentonite are presented in Table 2.

An analysis of the measured physicomechanical characteristics of the composites bearing bentonite shows that the optimum strain–stress characteristics are manifested by the composites containing 2 wt % organomodified bentonite. Note that an increase in the filler content leads to decreases in the ultimate tensile strength and in the relative elongation at break. Worsening of the properties when the optimum filler concentration is exceeded may be explained by an increase in the rigidity of molecules that interact with the filler within the amorphous phase and, hence, by an increase in brittleness and a reduction in strength. As the content of the active filler is increased, the internal strain and adhesion grow. A reduction in the internal strain can be achieved via modification of the filler surface with surfactants that facilitate an increase in the strength of bonds between the filler and polymer matrix particles [9]. The most popular modifiers for the treatment of layered silicates are cationic surfactants, most often ternary ammonium salts. For example, when triboengineering materials based on ultra-high-molecular-mass PE and kaolinite were developed, the filler was modified with cetyltrimethylammonium bromide; as a result, the strength increased by 17% and the relative elongation at break increased by 33% [10]. These results may be explained by the enhancement of the adhesion interaction in interphase layers between the filler and the polymer matrix.

Table 2. Physicomechanical and triboengineering properties of the composites bearing bentonite

| Bentonite content, wt % | ε , % | σ_u , MPa | I , mg/h | F |
|------------------------------|-------------------|------------------|------------|-----------|
| 0 | 351 | 21 | 125 | 0.04–0.20 |
| 2 | 310 | 23 | 0.7 | 0.15 |
| 5 | 330 | 20 | 0.08 | 0.20 |
| 7 | 250 | 17 | 0.07 | 0.20 |
| 10 | 228 | 14 | 0.08 | 0.21 |
| Bentonite modified with CTAB | | | | |
| 2 | 343 | 22 | 1.07 | 0.032 |
| 5 | 313 | 19 | 0.10 | 0.028 |
| 7 | 291 | 16 | 0.07 | 0.031 |
| 10 | 269 | 11 | 0.06 | 0.033 |

The wear resistances of the composites containing bentonite and organobentonite change insignificantly with their contents. However, the friction coefficients improved. For the composites bearing organobentonite, this parameter decreased by approximately an order of magnitude. This effect is associated with an increase in the adhesion interaction between the polymer matrix and the filler. For the composites with stronger interactions between the modified particles and the polymer matrix, the resistance to cyclic friction stress becomes much smaller. The separation of particles and small amounts of the polymer play a leading role in wear loss. Separate particles can act as

solid greases. This circumstance causes a reduction in the wear rate and friction coefficient [2].

The wear resistance of the composite containing 2 wt % organomodified bentonite increases by a factor of up to 116 relative to the wear resistance of the initial PTFE. As the filler content is increased to 10 wt %, the wear resistance increases by a factor of up to 2000 relative to that of the unfilled polymer, but the strength characteristics of the composites worsen substantially. A similar change in the behavior of PTFE is typical for the effect of conventional dispersed fillers that lead to the formation of microcomposites. After the introduction of various fillers into PTFE, antifriction properties usually worsen because, although the friction coefficient increases several times, the wear resistance grows [1]. For example, as was shown in [11], the introduction of carbon fiber into the composites with the friction coefficient in the range 0.26–0.30 entails an increase in the wear resistance by a factor of 85. It is known that the introduction of graphite, molybdenum disulfide, silicon dioxide, and titanium nitride into PTFE facilitates a reduction in the wear of polymer samples by a factor of more than 200 [12, 13]. At a friction coefficient of 0.10–0.22, the wear resistance may be increased by a factor of 100–370 after the introduction of synthetic ultradispersed ceramics and natural fillers (zeolites, diamond scrap) [14]. The authors of [14] demonstrated that the treatment of fillers with surfactants provides a substantial gain in the wear resistance of the composite materials, while the friction coefficient remains low.

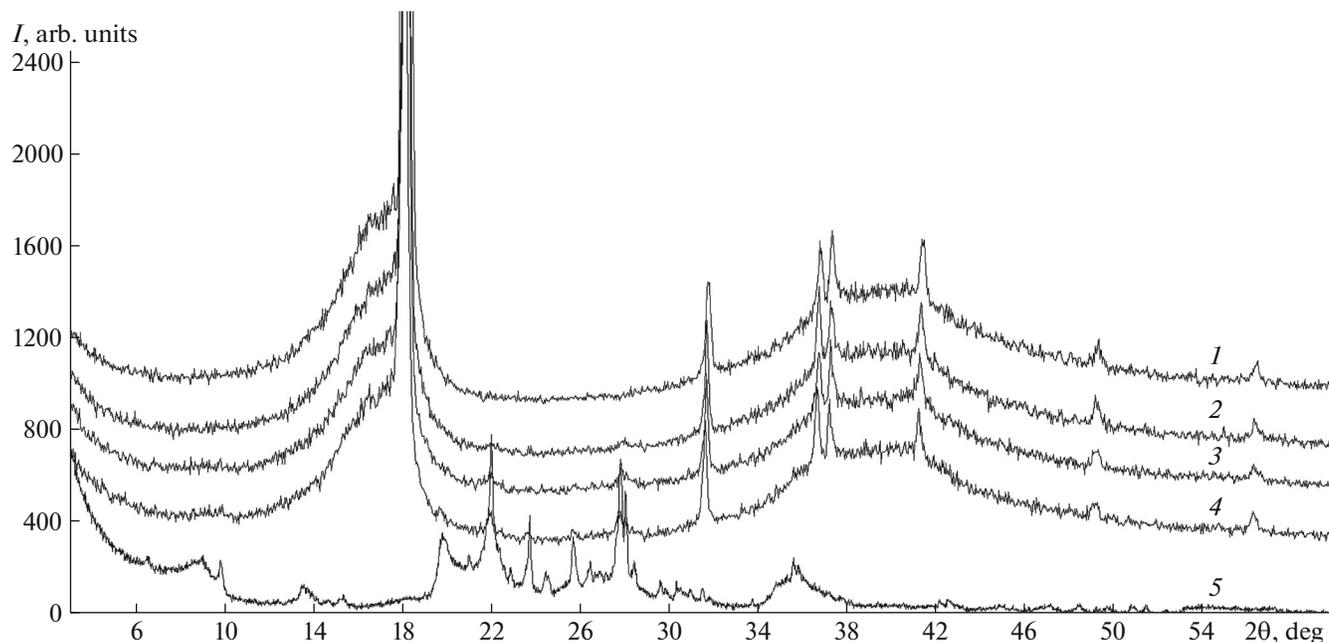
**Fig. 1.** X-ray patterns of (1) initial PTFE, (2) PTFE + 2 wt % bentonite + surfactant, (3) PTFE + 5 wt % bentonite + surfactant, (4) PTFE + 7 wt % bentonite + surfactant, and (5) bentonite modified with the surfactant.

Table 3. Degrees of crystallinity of the composites with organomodified fillers

| Filler | Filler content, wt % | α , % |
|-------------|----------------------|--------------|
| Vermiculite | 0 | 79 |
| | 2 | 68 |
| | 5 | 69 |
| | 7 | 70 |
| | 10 | 71 |
| Bentonite | 2 | 55 |
| | 5 | 59 |
| | 7 | 60 |

Vermiculite was modified with ADMBAC, and bentonite was modified with CTAB.

Figure 1 depicts the X-ray patterns of the initial organobentonite and the composites bearing organobentonite. It is obvious that the basal reflection of organobentonite features a broad low-intensity peak, a circumstance that may indicate high dispersity, defectiveness, and low crystallinity of the mineral.

To define the degree of intercalation of nanosilicate, the changes in the intensities and shapes of peaks corresponding to the initial components are used [15]. The formation of the exfoliated nanostructure, as a rule, is characterized by disappearance of basal reflections corresponding to nanosilicate, a phenomenon that testifies that the layers are considerably removed from each other [16]. In this case, the basal reflection

corresponding to the modified bentonite is retained in the composites (Fig. 1, curves 2–4). Moreover, there is displacement of basal reflection peaks to lower angles in the X-ray patterns of the composites, a result that might indicate formation of the intercalated structure. Although, for the composite bearing 7 wt % organobentonite (Fig. 1, curve 4), the basal reflection is not pronounced, the physicochemical and triboengineering parameters of this composite are not typical for the nanocomposite.

The X-ray patterns of the composites containing the organomodified vermiculite (Fig. 2, curves 2–5) show an intense basal reflection of the initial vermiculite ($2\theta \approx 8^\circ$ – 9°). Hence, the introduction of organomodified layered silicates in both cases leads to the formation of conventional microcomposites. The application of surfactants facilitates the improvement of adhesion interaction at the interface but appears to be insufficient for intercalation.

The resulting X-ray patterns were used to calculate the degrees of crystallinity of the composites (Table 3).

The degrees of crystallinity of the composites, as determined via X-ray diffraction, characterize the portion of regularly arranged molecules. An analysis of the X-ray data indicates that an increase in the filler content facilitates growth in the degree of crystallinity and, hence, in the fraction of regularly arranged molecules. The maximum degree of crystallinity, 71%, is observed for the composite bearing 10 wt % vermiculite modified with the surfactant. This dependence may be explained by the fact that modification of the layered silicate with the surfactant entails reduction in

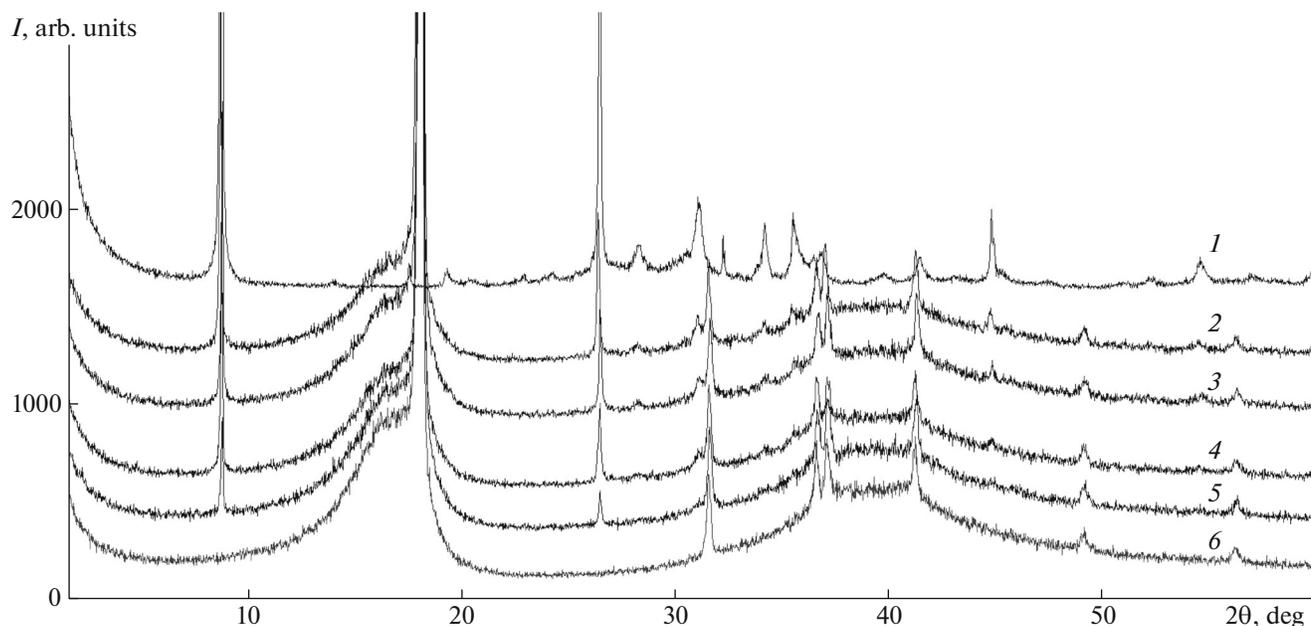


Fig. 2. X-ray patterns of (1) vermiculite modified with the surfactant, (2) PTFE + 10 wt % vermiculite treated with the surfactant, (3) PTFE + 7 wt % vermiculite treated with the surfactant, (4) PTFE + 5 wt % vermiculite treated with the surfactant, (5) PTFE + 2 wt % vermiculite treated with the surfactant, and (6) the initial PTFE.

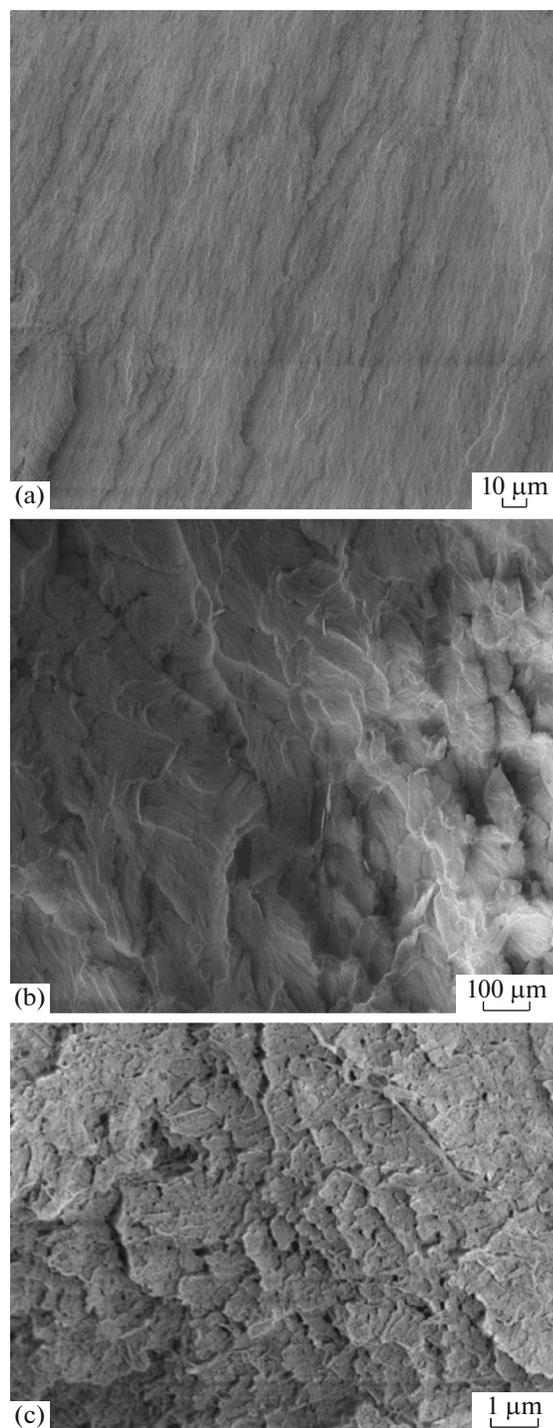


Fig. 3. Supramolecular structures of (a) initial PTFE, (b) PTFE + 2 wt % vermiculite modified with ADMBAC, and (c) PTFE + 2 wt % mechanically activated vermiculite.

the sizes of supramolecular polymer structures and leads to the formation of fine-grained crystalline structures.

In general, as the filler content is increased, the degree of crystallinity decreases [17] because the por-

tion of the polymer/filler interfacial layer and, accordingly, the portion of the amorphous fraction increase. During filling with layered silicates, the degree of crystallinity decreases on the whole; however, with an increase in the filler content, the degree of crystallinity tends to increase. This circumstance may be rationalized by the fact that an increase in the filler content causes agglomeration of layered silicate particles and, accordingly, a decrease in the effective area of inter-phase interaction.

Figure 3 shows the micrographs of the supramolecular structuring of the initial PTFE (Fig. 3a) and PTFE containing 2 wt % surfactant-modified vermiculite (Figs. 3b, 3c).

As follows from the comparison of the supramolecular structures of the composites, the modification of vermiculite with ADMBAC substantially affects the composite structure. For example, the composite bearing the ADMBAC-modified vermiculite features a more uniform structure than that containing simply mechanically activated vermiculite. During filling with the mechanically activated vermiculite in the absence of surfactant treatment, the supramolecular structure of the matrix becomes less than perfect, separate particles of vermiculite between the surface of the latter and the matrix are observed, and microcracks are formed. The mentioned changes in the morphology of the supramolecular structure of the matrix after the introduction of the mechanically activated vermiculite testify that the mechanical activation treatment of this filler is insufficiently effective.

Micrographs of friction surfaces of the composites containing the surfactant-modified vermiculite are presented in Fig. 4. The reorientation of structural elements of the material occurs along the sliding direction. During friction, silicate layers and a physical relief with chips and cracks form on the composite surface. As is clear from the micrographs, as the vermiculite content is increased, the cracks on the surface become smaller. Consequently, the SEM data confirm that the filler is localized on the surface during friction, a circumstance that hampers plastic deformation of surface layer of the polymer matrix and leads to a decline in the velocity of bulk wear.

Our studies show that the composites bearing CTAB-modified layered silicates feature better characteristics than those of the composites modified with ADMBAC. This result may be explained with allowance for the chemical formula of the surfactant. For example, CTAB has an alkyl chain consisting of 16 carbon atoms, whereas the alkyl chain of ADMBAC consists of 12 carbon atoms. As is known [3], for effective surface modification of a layered silicate, aliphatic chains of the surfactant must contain no less than 14 carbon atoms. Moreover, the steric effect of the surfactant occurs. The presence of a bulky benzyl radical near the reaction center, namely, the nitrogen atom, in the ADMBAC molecule may hinder the approach of

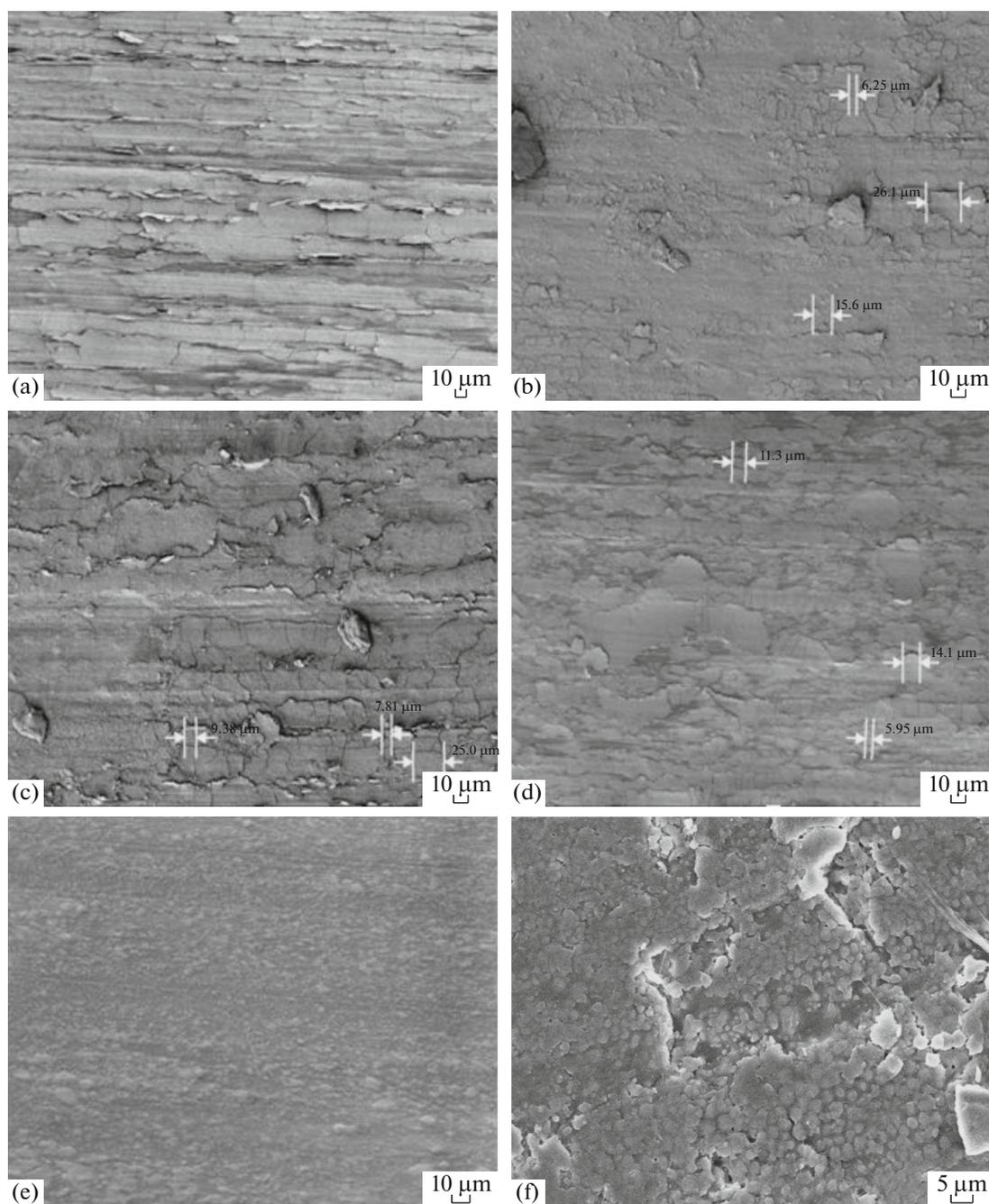


Fig. 4. Structures of the surface layers after friction: (a) PTFE + 2 wt % vermiculite with the surfactant, (b) PTFE + 5 wt % vermiculite with the surfactant, (c) PTFE + 7 wt % vermiculite with the surfactant, (d) PTFE + 10 wt % vermiculite with the surfactant, (e) initial PTFE, and (f) PTFE + 2 wt % vermiculite with the surfactant at 1000 \times magnification.

this atom toward cations of the layered silicate and, thus, may decelerate the cation-exchange reaction.

CONCLUSIONS

The effect of organomodified vermiculite and bentonite on the physicomechanical and triboengineering properties of PTFE has been studied. The modifica-

tion of layered silicates with surfactants somewhat worsens the strain–stress characteristics but improves the wear resistance of the material; simultaneously, its friction coefficient decreases. Our investigations have shown that the modification of layered silicates with surfactants improves the adhesion interaction between the polymer matrix and the filler, a circumstance that facilitates an increase in the triboengineering charac-

teristics but is insufficient for the formation of the intercalated structure. A comparison of the effects of CTAB and ADMBAC on silicate layers revealed that modification with CTAB leads to better parameters than does modification with ADMBAC. This result might be rationalized by the steric effect of the benzyl radical of ADMBAC, which overlaps the reactive center.

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