Effects of Surface Reactions during Friction on Tribological Characteristics of PTFE-Muscovite Composites

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Abstract. This work presents the results of tribological and structural investigations of polymer composites based on polytetrafluoroethylene and muscovite. It is shown that the wear resistance of the composites increased up to 675 times in comparison with the initial polymer. The increase of wear resistance is attributed to the occurrence of tribo-oxidation processes on the friction surface, which have been confirmed by various investigations. Thus, IR spectroscopy showed that carboxylate anions are formed on the friction surface of composites during friction processes. An increase in oxygen and a decrease in carbon and fluorine concentrations on the composite surface have been detected after friction using the EDS analysis. The results of XPS have confirmed the destruction of C-F bonds and the formation of new oxygen-containing compounds. These research methods indicated the occurrence of tribo-oxidative processes during friction.

1. Introduction

Nowadays polymers are widely used in various branches of human life, including the engineering industry, due to their strength, low density, weather, and corrosion resistance. One of the most widely used polymers is polytetrafluoroethylene (PTFE). PTFE is usually used as a solid lubricant and for manufacturing parts of friction units due to the low friction coefficient, corrosion, and thermal resistance. However, initial PTFE has some disadvantages such as poor wear resistance and creep. To improve its properties, fillers are added to the initial PTFE. Fillers reduce the slippage between the polymer lamellae, thus reduce the wear of materials [1]. Also, it is considered that the transfer film between the surface of the PTFE composite and counter body surface contributes to wear reduction.

The previously mentioned hypothesis is the main theory of wear reduction, but recently the new assumption has been suggested. According to this, the tribo-performance of PTFE composites is closely related to the chemical reactions between polymer surface and counter-body, the ambient air, the formation of metal fluoride bonding. Many researchers have found pieces of evidence in their studies [2-4]. At the same time, there is not enough discussion about the effect of the tribo-chemical reactions on the tribo-performance of the PTFE based composites.

Layered silicates as fillers have been used in our previous studies to investigate the role of filler on tribo-performance and tribo-chemical reactions [5]. Hence, the PTFE/layered silicate composites are
used in this work as the continuation of studies. The influence of tribo-chemical reactions on the tribo-performance will be analyzed and discussed. The objectives of this study are to investigate the effects of muscovite on the tribological behavior and wear mechanism of PTFE.

2. Experimental

The polymer matrix was polytetrafluoroethylene (PTFE) from Perm manufacture (Russia), trademark PN-90 (GOST 10007-80) with an average molecular weight 500000, an average particle size 90 μm, density 2150-2260 kg/m³. The analogue of PTFE PN-90 is Tarflen® SM-2 PTFE. PTFE was filled with natural layered silicate-muscovite KAl₂[AlSi₃O₁₀](OH)₂ was from the Kovdor deposit (Murmansk) with a Mohs hardness 2.5 – 3 and density 2760 – 3100 kg/m³. Magnesium spinel (MS) MgAl₂O₄ was synthesized at the Institute of Solid-State Chemistry and Mechanochemistry of the Siberian Branch of the Russian Academy of Science (Russia) using a mechanochemical method. MS has an average particle size of 70-80 nm and a specific surface of 170 m²/g and was used as a functional additive.

The preparation of muscovite included its drying at a temperature of 120 °C for 4 h. Then it was mechanically activated in the “Activator 2S” planetary mill (Russia) for 2 min. PTFE powder was provided with a particle size of approximately 90 mesh number. PTFE, muscovite, and magnesium spinel powders were mixed using a paddle mixer at 3000 rpm to make the mixture uniform and dispersive. After mixing, the uniform mixture was molded at 50MPa at room temperature for 2 min to prepare a sample. Then, samples were sintered in the laboratory oven at temperature 300-375 °C and cooled with rate of 0.03 °С / s. The amount of muscovite was varied in the interval 1 – 5 wt. %, and the amount of magnesium spinel was varied from 0.5 to 1 wt. %.

3. Results

Tribological properties of polymer composites were determined with the UMT-3 tribometer (CETR) at room temperature using a pin-on-disc friction scheme. Cylindrical specimens (10 mm diameter and 20 mm height) and a steel disk (brand 40X, HRC hardness 45 – 50) were used for the test. The applied load was 2 MPa, sliding speed 0.2 m/s, test duration 3 hours. Figure 1 shows the schematic representation of the pin-on-disc friction scheme. The rate of mass wear was evaluated by the weight loss of samples per time unit.

Energy dispersive spectroscopy (EDS) combined with scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and infrared spectroscopy (IR) analysis was used to determine the chemical composition of friction surfaces. A combination of XPS, EDS, and IR analysis can reveal plenty of useful information on processes and mechanisms which occur on a composite surface at friction. EDS test was conducted using the EDS X-MAX20 (Oxford) attachment of SEM microscope JEOL JSM-7800F. XPS data were obtained using K-Alpha (Thermo scientific) spectrometer, Al Kα emission with 100 W capacity, and 12 kV voltages. The diameter of the analysis field was 30 ~
400 μm. Fourier transform infrared spectroscopy (FTIR) analysis of composites surface was carried out using FTS 7000 Varian IR-spectrometer before and after friction.

4. Discussion

Table 1 shows the effect of the mica and MS concentration on the wear rate of PTFE composites. The results of the investigation showed that the introduction of MS increases wears resistance of the composites. As was confirmed by Okhlopkova et al. [6] the higher MS concentration corresponds to the better wear resistance. The mass wear rate of composites containing muscovite reduced by 600 times, composites with muscovite and MS – by 675 times.

| Muscovite content, wt. % | MS content, wt. % | I, mg / h | f  |
|--------------------------|-------------------|-----------|----|
| 0                        | 0                 | 120±5.50  | 0.20±0.01 |
| 0.5                      | 0                 | 4.18±0.20 | 0.24±0.01 |
| 0.1                      | 0.5               | 1.76±0.08 | 0.26±0.01 |
| 0.5                      | 1.0               | 9.50±0.45 | 0.18±0.01 |
| 1.0                      | 1.69±0.05         | 0.22±0.01 |
| 1.0                      | 0                 | 1.20±0.03 | 0.25±0.01 |
| 0.1                      | 1.84±0.05         | 0.23±0.01 |
| 0.5                      | 2.57±0.07         | 0.22±0.01 |
| 1.0                      | 3.79±0.10         | 0.18±0.01 |
| 2.0                      | 1.65±0.04         | 0.29±0.01 |
| 0.1                      | 1.43±0.03         | 0.26±0.01 |
| 0.5                      | 1.05±0.03         | 0.23±0.01 |
| 1.0                      | 0.78±0.05         | 0.23±0.01 |
| 5.0                      | 0                 | 0.45±0.01 | 0.29±0.01 |
| 0.1                      | 0.59±0.01         | 0.20±0.01 |
| 0.5                      | 0.43±0.01         | 0.23±0.01 |
| 1.0                      | 0.40±0.01         | 0.23±0.01 |

Note: MS – magnesium spinel, I – mass wear rate, f - friction coefficient.

It can be seen from table 1 that the friction coefficient increases with the increase of muscovite content. The migration of the mineral particles to the friction surface can explain the increase of the friction coefficient. The increase of the friction coefficient of the composite is negligible. According to the author’s previous investigations [7], the filler particles crop out to friction surface during the friction test and form a protective screen. These filler particles prevent destruction and wear.

The most significant influence on the mechanism of lubricating processes was given by the chemical interaction of composites with metal counter-body at severe conditions. As a result, films with lubricating properties are formed on both metal and composite friction surfaces [8].

To assess the effect of fillers on friction and wear processes composites surfaces were analysed by IR spectroscopy. The IR spectra of the composites, which have been recorded after friction in the range of 3600 – 2600 cm⁻¹, contain a wide absorption band. In accordance with the data from [9], such band in this range appears due to the formation of associated hydroxyl groups, moreover, the band corresponded to peroxides is also in this range. The presence of these bands in the spectra indicates the formation of the intermediate products of carbon chain oxidation. The appearance of these oxygen-containing groups serves as evidence of the participation of peroxide radicals in destruction reactions. 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 counter-body material. This is confirmed by the presence of two characteristic peaks in the range of 1680 – 1400 cm⁻¹.
cm\(^{-1}\) in the IR spectra of all composites (figure 2). It is possible that the formation of carboxylates favours 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 destruction of polymer macromolecules is high because radical particles will react with each other to form a new bond or, in this case, a cross-linking and thus will create a secondary wear-resistant layer on the surface of friction.

![FTIR spectra](image)

**Figure 2.** FTIR spectra of: (a) initial PTFE, (b) muscovite-PTFE composites before and after friction.

As shown in figure 2 (a), the initial PTFE exhibits transmittance bands at 1201, 1146, and 636 cm\(^{-1}\) corresponding to C-F stretching in –CF\(_2\)- groups of PTFE. The bands corresponding to wagging vibrations \(\gamma_{\omega}\) (CF\(_2\)) are transmittance at 639 cm\(^{-1}\). Besides, new broad peaks at 3285, 1648, and 1414 cm\(^{-1}\) were observed in the spectrum after friction, see figure 2 (b). There are not these new peaks in the spectra of not worn surfaces of both PTFE and composite. The broadband at 3400 cm\(^{-1}\) corresponds to the stretching vibration of the hydroxyl bonds of associated with the carboxylate salts water [9]. The bands near 1648 and 1414 cm\(^{-1}\) were assigned to the antisymmetric and symmetric oscillations of two equivalent C=O bonds [10]. Pitenis et al. have revealed these carbonyl groups are generated tribo-chemically and are part of carboxyl groups of perfluorinated carboxylic acids chelate salts [9]. This can occur due to the destruction of PTFE by different mechanisms. Because PTFE has a high molecular weight (~500000), it can be assumed that the whole chain of PTFE cannot be transferred to the metal counter-body during friction, therefore the PTFE chain can be split [11]. Also, it should be taken into account that one of the specimen preparation process stages usually is conducted in the presence of oxygen and it gives reason to assume that the PTFE could be oxidized during friction. Similar hypothesis has been reported by Pitenis et al. in [9], where they have supposed that terminal carboxylate groups are generated by the tribo-chemical breaking of C-C bonds in the presence of a favourable environment with water vapor. Harris, Kajdas et al. [11-12] attribute the broad peaks at 1650, 1432 cm\(^{-1}\) observed in the IR spectrum of PTFE / Alumina composites to carboxylic acid end groups. The appearance of these peaks coincides with carboxylate peaks in the XPS spectra.

Furthermore, heat generation contributes to the change of sample structure. All the above-listed factors lead to the cross-linking of separate fragments of macromolecules thermo-oxidative decay and forming cross-linked structure with high wear resistance.
As can be observed in figure 3, the spectrum of worn composite surface contains peaks of chromium and iron which most likely were transferred from counter-body. Also, oxygen content increases while carbon and fluorine concentrations decrease (Figure 3, Table 2).

![Figure 3. EDS analysis of muscovite-PTFE composite: (a) initial surface (b) worn surface](image)

**Table 2.** EDS analysis of muscovite-PTFE composites before and after friction

| Element | Initial surface | Worn surface |
|---------|----------------|--------------|
|         | Weight, %       | Atomic, %    | Weight, %       | Atomic, %    |
| C       | 17.09           | 24.57        | 16.96           | 25.01        |
| O       | 3.06            | 3.31         | 7.53            | 8.33         |
| F       | 77.87           | 70.79        | 68.78           | 64.13        |
| Mg      | 1.21            | 0.86         | 0.57            | 0.42         |
| Si      | 0.76            | 0.47         | 0.40            | 0.25         |
| Cr      | -               | -            | 0.97            | 0.33         |
| Fe      | -               | -            | 4.79            | 1.52         |
| Total   | 100.00          | 100.00       |

XPS spectra of the lines F1s and C1s recorded for the PTFE and PTFE with 1 wt. % muscovite composite after friction in figure 4. The initial PTFE has the position and shape of the F1s line at 688.3 eV and C1s at 291.8 eV that correspond to groups CF$_2$-CF$_2$ [13]. After the friction process, the new peak of O1s line at 531.4 eV was found. The presence of oxygen after friction indicates the occurrence of the destruction of the polymer during friction in oxygen-containing environment. Peaks assigned to C-F (291.7), -COO- (~288.7) and C or C-C (284.6 eV) are detected on the worn composite surface [14]. The peak at ~289 eV complies with the R-COOH group [9]. These facts confirm the destruction of the polymer, the decrease in fluorine content on the surface, and hence, the formation of C–C bonds and carboxylate anion. According to Zuo experiment [3] the activation energy of PTFE defluorination is only about 1.0 kcal/mol, and it means defluorination is high-probability process
during friction. Besides the peak at 687.9 eV, the new peak at ~683.5 eV was detected in the XPS spectra of the composite. It corresponds to the existence of metal–F bonds according to the researchers [15, 16]. This assumption about the formation of Al-F and Fe-F bonds during friction was reviewed in [17, 18]. In Gao et al., studies [4] a possible mechanism of chemical reactions that proceed on the surface of PTFE and metal counter-body was described. Gao suggested the formation of metal–F bonds via radical reactions.

Figure 4. XPS spectra of specimens of (a)–(b) PTFE and (c)–(e) PTFE + 1 wt % of muscovite composite subjected to friction: (a) C1s; (b) F1s; (c) C1s; (d) F1s; and (e) O1s

5. Conclusion
The tribological tests of composites based on PTFE have shown that the PTFE destructs during friction and new terminal carboxyl groups formed at the presence of ambient air. It means that the tribo-chemical reactions take place on the friction surface of PTFE and its composites and these carboxyl groups are formed by breaking of C-C bonds. The IR spectroscopy and XPS have confirmed PTFE macromolecules break during friction. Also, XPS detected Me-F chemical bonds on surfaces of PTFE and its composites after friction.

Thus, the formation of the wear resistant surface of composites is a complex process that involves chemical reactions between components of composite, metals of counter-body, filler particles and the presence of atmospheric oxygen and water vapor.

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References
[1] Friedrich K 1986 Friction and Wear of Polymer Composites vol 1 (Amsterdam: Elsevier Science Publishers) p 478
[2] Gong D L, Zhang B, Xue Q J, Wang H L 1990 Wear 137 pp 267–273
[3] Zuo Z, Yang Y, Qi X, Su W, Yang X 2014 Wear 320 pp 87-93
[4] Gao J T 2000 Wear 245 pp 100-106
[5] Sleptsova S A, Okhlopkova A A, Kapitonova Iu V, Lazareva N N, Makarov M M, Nikiforov L
A 2016 *J. Fric. Wear* **37** pp 129-135

[6] Okhlopkova A A., Popov S N, Sleptsova S A, Petrova P N, Avvakumov E G 2004 *J. Struct. Chem.* **45** pp 172-177

[7] Kirillina I V, Nikiforov L A, Okhlopkova A A, Sleptsova S A, Yoon C, Cho J H 2014 *Bull. Korean Chem. Soc.* **35** pp 3411-3420

[8] Zhang Z, Xue Q, Liu W, Shen W 1997 *Wear* **210** pp 151-156

[9] Pitenis A A, Harris K L, Junk C P, Blackman G S, Sawyer W G, Krick B A 2015 *Tribol. Lett.* **57** p 4

[10] Nakanishi K 1962 *Infrared absorption spectroscopy: practical* (San Francisco: Holden-Day) p 243

[11] Harris K L, Pitenis A A, Sawyer W G, Krick B A, Blackman G S, Kasprzak D J, Junk C P 2015 *Macromolecules* **48** pp 3739−3745

[12] Kajdas C K 2005 *Tribol. Int.* **38** pp 337-353

[13] Wheeler D 1980 *NASA Tech. Pap.* **1728**

[14] Shen J T, Top M, Ivashenko O, Rudolf P, Pei Y T, De Hosson J Th M 2015 *Appl. Surf. Sci.* **331** pp 482-489

[15] Cadman P, Gossedge G M 1979 *Wear* **54** pp 211–215

[16] 1979 *Handbook of X-ray photoelectron spectroscopy*, ed by Wagner C D, Riggs W M, Davis L E, Moulder J F, Muilenberg G E (Minnesota: Perkin-Elmer Corporation) p 190

[17] Gong D L, Xue Q J, Wang H L 1991 *Wear* **148** pp 161–169

[18] Suzuki M, Prat P 1999 *Wear* **225** pp 995–1003