Properties and Structure of the Friction surface of PTFE / Layered Silicate Composites

S A Sleptsova¹, S Laukkanen¹, P N Tarasova¹

¹North-Eastern Federal University, Belinskiy str., 58, Yakutsk, 677000, Russia

E-mail: ssard@yandex.ru

Abstract. The wear of PTFE filled with layered silicates (LS) was investigated depending on the concentration and chemical nature of the fillers. The influence of these factors on the tribotechnical characteristics and the structure of the surface layers of composites is shown. Using SEM methods, it has been established that the introduction of LS contributes to the formation of a protective layer on the friction surface consisting of worn PTFE particles and a filler. The thickness of the layer does not depend on the concentration of LS, and the structure of the layer varies depending on the chemical composition of the fillers. It is shown that the formation of a protective layer occurs by means of worn particles clustering, uniformly covering the friction surface layer by layer.

1. Introduction

At present, one of the most developed theories of friction is the combined molecular-mechanical or adhesion-deformation theory of friction, the founders of which were B.V. Deryagin, I.V. Kragelsky, F. Bowden, D. Teybor [1, 2], according to which the friction process consists of interrelated processes: deformation of contacting asperities and molecular interaction of materials on the actual contact spots. Irregularities experience elastic, plastic, viscoelastic deformation depending on the properties of materials, as well as microcutting. Deformation is accompanied by mechanical energy dissipation, which is determined by the type of deformation, friction conditions, the properties of the contacting materials, the large-scale level of mechanical properties, the composition of the environment, and other factors. The appearance of each defect entails a corresponding change in the general state of the surface layer, characterized by internal energy and entropy. According to thermodynamics, the surface layer can be considered as an open thermodynamic system that is capable to exchange energy and matter with the environment and characterized by a complex of intense characteristics. However, such models do not take into account the fact that during the deformation process self-organizing dissipative processes are activated, as a result of which, before destruction, highly ordered structures are observed in the deformable material instead of the expected chaos and degradation, i.e. entropy formed during the accumulation of defects is continuously pumped out of the system [3].

Frictional transfer under friction without a lubricant practically takes place in any conditions and modes of friction [4] and one of the consequences of the formation of transfer films is the effect of self-lubrication. However, the self-lubricating effect is characterized not only by the presence of a strong transfer film, but also by the presence of a lubricating polymer layer that is shifted relative to the counterbody and the friction part [5]. In order for the polymer to provide lubrication it is necessary that it can withstand the dynamic loads caused by the applied load and frictional shear stresses. If this
condition is fulfilled various friction mechanisms may arise depending on the types of polymer, fillers and friction conditions. To ensure the best slip it is necessary to form a “shear layer” between the rubbing surfaces. Such a shear layer is necessary to reduce the adhesion and various “plowing” interactions that occur between surfaces moving relative to each other. It was found that the thinner the layer the better the sliding friction is ensured.

Thus, to realize the effects of self-lubrication and self-organization of the structure of polymer composites during the process of friction and wear, it is necessary to select combinations of material components in such a way as to ensure the lability of the structural elements of the polymer to facilitate the structuring process in the process of frictional loading. Achieving the response of materials to external influences can be implemented in nanocomposites - materials containing nanoscale modifiers and fillers. Layered silicates, known as clays, turned out to be promising nanometer dispersion fillers for the production of thermoplastic nanocomposites.

The aim of the work is to study the effect of layered mineral silicates on the tribological properties and the structure of the friction surface of PTFE composites.

2. Materials and methods of research

PTFE of the PN grade (GOST 10007-80) was chosen as the polymer matrix. Natural layered silicates (LS) (Tables 1 and 2), as well as nanodispersed magnesium spinel (MS) were chosen as fillers.

Table 1. Classification and deposit of used layered silicates.

| Mineral   | Classification                        | Deposit               |
|-----------|---------------------------------------|-----------------------|
| Kaolinite | mineral, aluminum hydrosilicate       | Glukhovetske, Ukraine |
| Serpentine| magnesium hydrosilicate mineral       | Rikolatva, Murmansk region |

Table 2. Characteristics of layered silicates.

| LS         | Structural formula | Laying Type | Cations in tetrahedra | Octahedron cations | Interlayer cations |
|------------|--------------------|-------------|----------------------|--------------------|--------------------|
| Kaolinite  | Al₂[Si₂O₅](OH)₄  | 1:1         | Si⁴⁺                 | Al³⁺               | -                  |
| Serpentine | Mg₃[Si₂O₅](OH)₄  | 1:1         | Si⁴⁺                 | Mg²⁺               | -                  |

Synthetic magnesium spinel (MS) is a double oxide with the general chemical formula MgAl₂O₄ obtained by the mechanochemical method at the Institute of Solid State Chemistry and Mechanochemistry of the SB RAS (Russia). The feature of the MS is a high dispersion (particle size is about 70-80 nm) and a developed specific surface area (170 m² / g) (Table 3).

Table 3. Characteristics of magnesium spinel [6].

| Formula   | Average particle size (nm) | Specific surface (m² / g) | Density (kg / m³) | T_melting (° C) |
|-----------|---------------------------|--------------------------|-------------------|-----------------|
| MgAl₂O₄   | 75                        | 170                      | 3600              | 2135            |

The preparation of the LS consisted of drying in a drying oven with subsequent mechanical activation. Temperature mode of drying: 6 hours at 105-120 °C, except vermiculite, which was subjected to heat treatment at 950 °C for 3 seconds. For the samples of composites used the original LS, as well as the activated LS, activated MS was injected into some of the composites. Mechanical activation of fillers was carried out in an Activator 2S planetary mill (Russia) for 2 minutes at a drum rotation speed of ω = 2500 rpm (centrifugal acceleration developed by grinding bodies g = 150 m·s⁻¹). To determine the optimal mode of mechanical activation, we analyzed such LS characteristics as dispersity and specific surface area before and after mechanical activation. Composites were obtained by dry mixing in a paddle mixer. Next, the samples were molded by cold pressing and sintered in the range of 370–380 °C. The tribotechnical characteristics of the composites (mass wear rate and friction coefficient)
were determined according to GOST 11629-75 on the universal high-temperature tribometer UMT-3 (CETR, USA) according to the “pin-on-disk” friction scheme at a load of 2 MPa and sliding speed of 0.25 m/s. The samples for the tribotechnical study had the shape of a cylinder with a diameter of 10 mm and a height of 20 mm. The counterbody was a disk made of steel 45 with a hardness of 45-50 HRS and a roughness of Ra = 0.06-0.07 μm. Samples were worn in 2 stages: during the run-in period and after it. After the end of the run-in period the change in mass of the sample was measured using a Mettler Toledo scale (±10 μg), the counterbody was cleaned with ethanol and samples were worn for 5 hours again. The friction coefficient was determined automatically by the program CETR Data Viewer 2.1. The study of the friction surface of composites was performed on the SEM “JSM-6480LV” and “JSM-7800F” (JEOL, Japan).

3. Experimental results and discussion
The run-in process plays an important role in the study of the tribotechnical characteristics of composite materials, since the durability and reliability of engineering polymer materials and coatings depend on it. It is known that the conditions for the transition of the system to processes with a minimum energy cost of friction under steady state conditions are created at the initial stage of friction. The run-in wear without lubrication does not take place over the entire area of the material, but only along the contacting protrusions of the irregularities of surfaces friction pair and is accompanied by complex irreversible phenomena occurring in the surface layer [2]. The test of wear performance of the PTFE/LS composites shows that the introduction of LS significantly increases the wear resistance of PTFE (see Tables 4 and 5) up to 1000 times. The introduction of even 2 wt.% LS reduces the wear of PTFE from 300 to 600 times. It was revealed that the additional introduction of MS positively affects the wear resistance of composites containing kaolinite and serpentine. The introduction of MS contributes to some reduction in the friction coefficient of the composites. The wear resistance of composites depends on the ratio of LS and MS - in composites with serpentine, an increase in the MS content leads to a reduction in the run-in period and a faster transition of the system to a stationary friction mode.

Table 4. Tribomechanical characteristics of PTFE / Serpentine composites depending on the content of magnesium spinel.

| The content of fillers (wt.%) | $I_{\text{run-in}}$ (mg/h) | $I_{\text{st,}}$ (mg/h) | Friction coefficient $f$ |
|-----------------------------|--------------------------|------------------------|------------------------|
| Serpentine  | MS |  |  |  |
| 0  | 0 | 112.48±3.37 | 65.6±1.96 | 0.23±0.007 |
| 2.0 | 0 | 1.75±0.05  | 0.10±0.003 | 0.32±0.009 |
| 1.5 | 0.5 | 0.77±0.02 | 0.16±0.005 | 0.25±0.007 |
| 1.8 | 0.2 | 0.85±0.02 | 0.10±0.003 | 0.24±0.007 |
| 5.0 | 0 | 0.59±0.01 | 0.14±0.004 | 0.32±0.009 |
| 4.0 | 1.0 | 0.35±0.01 | 0.14±0.004 | 0.26±0.008 |
| 4.5 | 0.5 | 0.91±0.02 | 0.13±0.004 | 0.26±0.008 |
| 4.8 | 0.2 | 0.95±0.03 | 0.10±0.003 | 0.27±0.008 |
Table 5. Tribomechanical characteristics of composites PTFE / Kaolinite depending on the content of magnesium spinel.

| The content of fillers (wt.%) | \( a I_{\text{run-in}} \) (mg/h) | \( b I_{\text{s}} \) (mg/h) | Friction coefficient \( f \) |
|------------------------------|-------------------------------|-------------------------|------------------|
| Kaolinite                   | MS                            |                         |                  |
| 0                            | 0                             | 112.5±3.37              | 65.6±1.96        | 0.23±0.007       |
| 2.0                          | 0                             | 1.92±0.06               | 0.23±0.007       | 0.33±0.009       |
| 1.5                          | 0.5                           | 0.98±0.03               | 0.13±0.004       | 0.24±0.007       |
| 1.8                          | 0.2                           | 1.14±0.03               | 0.18±0.005       | 0.22±0.006       |
| 5.0                          | 0                             | 0.77±0.02               | 0.12±0.003       | 0.32±0.009       |
| 4.0                          | 1.0                           | 1.56±0.04               | 0.15±0.004       | 0.27±0.008       |
| 4.5                          | 0.5                           | 0.21±0.006              | 0.13±0.004       | 0.27±0.008       |
| 4.8                          | 0.2                           | 0.49±0.01               | 0.09±0.002       | 0.23±0.007       |

\( a I_{\text{run-in}} \) - the rate of mass wear during the run-in period.
\( b I_{\text{s}} \) - the rate of mass wear during the steady state period.

However, a higher level of wear resistance of the material in the steady-state friction mode was provided by a low MS content. In the case of composites with kaolinite the presence of an optimal MS content is revealed, which contributes to a more rapid transition of the system to a stationary mode, and its minimum wear in this friction mode.

It is known that the run-in stage is characterized by smoothing of microroughnesses and the establishment of optimal surface roughness, accompanied by plastic deformation of the surface layers, loosening and amorphization of the material structure. These processes, along with high temperature, lead to the formation of a secondary structure layer on the friction surface, which differs in its physicomechanical, physicochemical and thermophysical properties from the rest of the composite material [6]. In [7] it is assumed that the new structure is similar to the structure of thermotropic liquid crystals. The authors believe that this can explain the ease of sliding of the sublayers and the multiple increase in the wear resistance of the surface layer. In this case, the chemical composition and structure of the surface layer also, as a rule, usually differ from the supramolecular structure of the composite itself [8, 9]. A feature of composites containing LS is the formation on the friction surface of a thin surface layer, even visually differing in consistency from the material itself (Fig. 1). Judging by microphotographs (Fig. 1), the consistency of the layer resembles a finely divided mass and plays the role of a solid lubricant that protects the surface of the material from abrasion. The layer is obviously formed mainly from wear particles that appear in large quantities at the beginning of abrasion and fall onto the friction surface [10].

![Figure 1. The formed secondary structure layer on the friction surface of composites with kaolinite: a - side view, the arrow shows the layer (x3000); b - top view (x1000).](image-url)
In [10], a diagram of the formation of a protective layer on the surface of PTFE modified with nanodispersed aluminum oxide is presented. As the authors note, the circulation of wear products between the transfer film on the counterbody and the layer on the friction surface of the composite is the key to a high cycle of maintaining ultra-low wear of composites based on PTFE and nanosized alumina.

That is, wear particles falling over and over again on the friction surface undergo mechanochemical processes of dispersion, defragmentation, activation, and oxidation. At the same time, the friction surface is enriched with particles of silicates, which are oriented along the direction of friction. When moving under load on rubbing surfaces, layered substances, for example, graphite, are able to orient themselves so that the main axes become parallel to the sliding direction [11]. The forming protective layer, due to the particles of silicates contained in them, has low shear resistance, respectively and is able to slip relative to the surface of the counterbody and the surface of the composite in the direction of shear. In addition, due to plasticity, the protective layer smooths the friction surface, filling cavities and irregularities, as well as leveling microprotrusions and the microroughnesses of the friction surfaces.

The surface layer of composites containing serpentinite and kaolinite does not visually differ significantly from the surface layer of composites containing additional MS (Fig. 2).

Figure 2. Microphotographs of the composite's friction surface: a - with 2.0 wt.% kaolinite; b - with 1.8 wt.% kaolinite and 0.2 wt.% MS; c - with 2.0 wt.% serpentinite; d - with 1.8 wt.% serpentinite and 0.2 wt.% MS. A magnification of 500 times.

However, the friction surfaces of composites without MS can be characterized as looser, and the friction surfaces with MS as denser and even. This circumstance may confirm the assumption about the reason for the change in the friction coefficients of these composites.

4. Conclusions

Thus, an analysis of the results of studying the friction surface of composites by SEM showed that the key role in the formation of the protective layer is in the circulation of material wear particles, which is accompanied by mechanochemical processes with their active participation.

Due to the presence of active metals in the composition of LS and MS, the formed protective layer on the friction surface is quite strong, but at the same time, due to silicon oxide and PTFE particles, it has the necessary plasticity, which allows the layer to maintain lability and maintain high wear resistance, localizing contact deformations and preserving thereby the main material. The peculiarity of LS as components of a tribochemical material lies in their ability to easily disperse, creating a protective layer of a secondary structure of optimal thickness on the friction surface, regardless of the concentration of fillers.

5. References

[1] Frolov K V 2008 Modern Tribology: Results and Prospects (Moscow: Publishing House of LKI) p. 476 (In Russian)
[2] Bowden F P and Tabor D 2001 The Friction and Lubrication of Solids (Oxford: Clarendon Press) p. 374
[3] Berkovich I I and Gromakovsky D G 2000 Tribology. Physical foundations, mechanics and technical applications: Textbook for high schools ed. D.G. Gromakovsky (Samara: Samar. state tech. University) p.268 (In Russian)

[4] Myshkin N K, Petrokovets M I, Kovalev A V 2005 Tribology of polymers: adhesion, friction, wear, and mass-transfer. Tribol. Int. 38 pp 910-21

[5] Fusaro R L 1990 Self-lubricating polymer composites and polymer transfer film lubrication for space applications Tribol. Int. 23(2) pp 105–22

[6] Sawyer W G, Argibay N, Burris D L, Krick B A 2014 Ann. Rev. Mater. Res. 44(1) pp 395–427

[7] Mashkov Yu K, Ovchar Z N, Baybaratskaya M Yu, Mamaev O A 2004 Polymer composite materials in tribotechnology (Moscow: Nedra-Business Center) p. 262 (In Russian)

[8] Belyi A V, Karpenko G D, Myshkin N K 1991 Structure and methods of formation of wear-resistant surface layers (Moscow: Mashinostroenie) p 208 (In Russian)

[9] Okhlopkova A A and Sleptsova S A 2003 Mech. Compos. Mater. 39 (2) pp 123-8

[10] Harris K L, Pitenis A A, Sawyer W G, Krick B A, Blackman G S, Kasprzak D J and Junk C P 2015 Macromolecules 48 pp 3739–45

[11] Kostetsky B I 1970 Friction, lubrication and wear in machines (Kiev:Technique,) p 396 (In Russian)

Acknowledgments
This research was supported by the Ministry of Science and Higher Education of the Russian Federation under grant agreement No. FSRG-2020-0017.