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Article

Effect of Magnesium Spinel on the Properties and Structure of Composites PTFE/Layered Silicate

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Abstract: The article describes the study of the properties of polytetrafluoroethylene, modified using natural layered silicates - serpentinite. It is shown that the introduction of a small amount of layered silicates significantly increases the tribological characteristics of the material. The additional introduction of magnesium nano-spinels facilitated the formation of an intercalated polymer-silicate nanocomposite.

Keywords: polymer composites, polytetrafluoroethylene, fillers, layered silicates, serpentinite, wear resistance, strength, interfacial interaction.

1. Introduction

One of the most promising approaches to the development of polymer nanocomposites is the use of layered silicates as fillers of polymers, which are widely distributed and are well known as clay minerals. A significant improvement in the properties of the original polymers is achieved in the case of intercalation of polymer macromolecules in the interlayer space of silicates, followed by exfoliation into individual nanolayers dispersed in the polymer volume [1, 2]. Concerning the development of tribological materials, interest in layered silicates as fillers of a polymer matrix arises in connection with the prospect of creating self-lubricating polymer nanocomposites. Also, it should be mentioned [3, 4] that with the addition of even a small amount of clay (2-3 wt.%) to the polymer matrix, the coefficient of thermal expansion significantly decreases. Layered natural inorganic structures such as montmorillonite, hectorite, vermiculite, kaolin, saponite [5], etc., are used to create polymer-layered nanocomposites. Most of the natural layered silicates commonly used in nanocomposites as nanoscale particles belong to the family of structure types 2:1 (Fig.1, a). In layered silicates with similar structure, the octahedral layer is enclosed between two layers of silicon-oxygen tetrahedrons. In tetrahedron, trivalent aluminium replaces part of the tetravalent silicon. As a result, a negative charge is formed on the layer, which is compensated by hydrated cations of alkali or alkaline-earth metal enshrined between the layers [6]. A partial positive charge, formed on each cation inside the gallery, gives the layered silicates hydrophilicity. This feature of silicates of the 2:1 structure makes it possible to exhibit them as the most effective modifiers for polar polymers, such as polyamide [7, 8]. So far polymer-layered nanocomposites with nonpolar or weakly polar polymers are not considered to have such high operational characteristics as materials based on polar polymers [9, 10]. There is no information on the effect of such kind of fillers on the change in the properties of composites based on PTFE. First of all, this is due to hydrophilicity of the given silicates - the main problem of incompatibility with an organic polymer matrix. To solve this problem, researchers often modify layered silicates with surfactants by replacing inorganic cations within silicate layers with organic cations. Substitution by cationic surfactants, such as bulk ammonium and phosphonium ions, increases the space between the layers, reduces the surface energy of the clay, and imparts a hydrophobic character to the clay surface [11, 13]. It should be noted that in the case of using layered silicates as fillers of the non-polar polymer matrix as PTFE, their surface modification using surfactants is ineffective because surfactants do not withstand the temperature conditions of PTFE processing (375 - 380 °C).

A promising way to improve the compatibility of layered silicates to the polymer matrix is the use of mechanical activation methods. Several papers confirm the effectiveness of these methods [13, 14]. The authors of this paper showed the effect of activated layered silicates, vermiculite (structure 2:1) and serpentinite (structure 1:1), on the characteristics of PTFE in [15]. Nanosized magnesium spinel was additionally introduced into the composite mixtures to increase the strength characteristics of the composites. It was shown that the introduction of magnesium nanospinel contributed to a significant increase in the wear resistance of composites; however, an increase in tensile strength was observed only in composites with serpentinite. The structure of the crystal lattice 1:1 means that for one silicon-oxygen tetrahedral layer there is one octahedral (Fig.1, b). In this case, the charge of octahedron entirely compensates the charge of the tetrahedron [6]. Consequently, serpentinite does not have hydrophilicity. These data may indicate the effect of the type of lattice structure of layered silicates on their compatibility with PTFE and on the formation of composites.

In this paper, an attempt has been made to improve the compatibility of serpentinite with PTFE more effectively by using active nanosized compounds as modifiers of serpentinite.

The purpose is to study the combined effect of mechanically activated serpentinite and nano-dispersed spinel on the properties of PTFE.

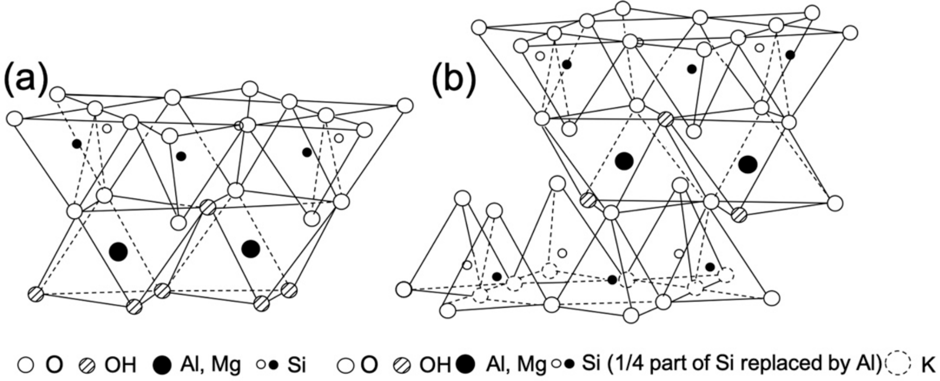

Fig. 1. Crystal lattice of types 1:1 (a) and 2:1 (b)

2. Materials and Methods

The objects of the study were polymer composite materials based on grade Mo PTFE (GOST 10007-80), with density 2150-2190 kg/cm^3, modified by natural layered silicate - serpentinite and composites containing mechanically activated serpentinite and magnesium nanospinel. The serpentinites are magnesium hydrosilicates of general formula $Mg_6[Si_4O_{10}](OH)_8$, formed by alteration of olivine rocks. They consist mainly of serpentine group minerals mixture: fibrous chrysotile, plate-shaped antigorite and massive lizardite, and according to the prevailing mineral composition, the antigorite, chrysolite, lizardite serpentinites are distinguished respectively [16]. Serpentinite used in this work refers to the antigorite. The unit cell consists of two layers: the first layer is a grid of silicon-oxygen tetrahedra with the general formula of a grid $[(Si_2O_5)(OH)]$, and the second layer is laid out with brucite octahedra $[Mg(OH)_2]$ (fig. 2).

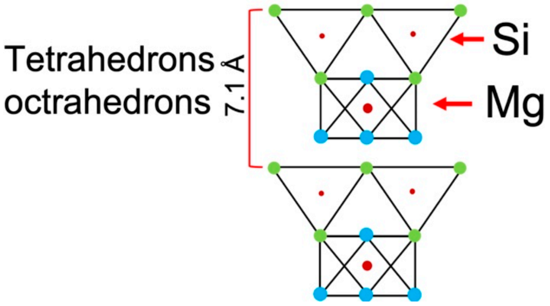

Fig. 2. The side view of the 1:1 structure of serpentinite:

Magnesium nano-spinel (NMS) is a complex compound with the general formula $MgO \cdot Al_2O_3$. It is a solid interstitial solution obtained by the plasma-chemical method in the Institute of Solid State Chemistry and Mechanochemistry SB RAS (Novosibirsk). The average particle size is 70-90 nm, the specific surface area is 170 m^2/g. Serpentinite was dried in an oven at 120 °C for 6 hours to remove adsorbed water completely. The dried serpentinite was activated in a planetary type mill "Activator-2S» (Russia) for 2 minutes with the speed of drums 2000 rpm. NMS was introduced into the mechanically activated powder of serpentinite. Composites were prepared by dry mixing polymer with filler, using cold moulding technology followed by free sintering.

Mechanical properties of composites are characterised by an elongation at break, tensile strength and elastic modulus using standard techniques (GOST 11262-80); they were tested in machines "UTS-2" (Germany), Shimadzu AGS-J (Japan) at room temperature and velocity of the movable grippers was 100 mm/min. The wear rate and the coefficient of friction were determined on a friction machine SMC-2 (Russia) according to the friction scheme "shaft-bush", at the load of 0.45 MPa, and sliding speed 0.39 m/s (GOST 11629-75). SEM, IR spectroscopy and XRD were used for structural studies. Micrographs of chipping and friction surface of polymer composites with energy dispersive microanalysis were obtained in a scanning electron microscope Jeol JSM-78000F (Japan). Low-temperature brittle chips were prepared by the destruction of samples at the temperature of liquid nitrogen. The electrically conductive structureless film of 10 nm thick was created by vacuum deposition of gold. IR spectra were recorded using a Varian FTS 7000 Fourier-step-scan spectrometer (USA). X-ray diffraction patterns were obtained using diffractometer ARL X'TRA (Switzerland) with Cu$K\alpha$ radiation (λ=1.5405 Å) under scanning in increments of 0.04° and the accumulation time at each point within 3 s. Values of cation exchange capacity (CEC) were investigated according to GOST 21283-93 using methylene blue.

3. Results and discussion

Analysis of mechanical and tribological characteristics (Fig. 3 and 4) demonstrates that composites comprising simultaneously serpentinite and magnesium nano-spinel exhibit the highest values of strength and wear resistance characteristics.

These figures (Fig. 3, 4) show the nature of the effect of fillers on the properties of composites.

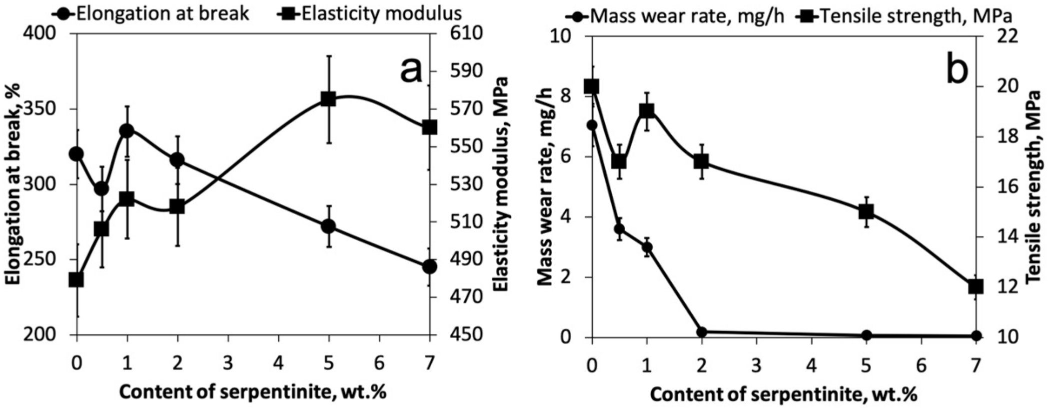

Fig. 3. Mechanical and tribological characteristics of composites depending on the content of serpentinite.

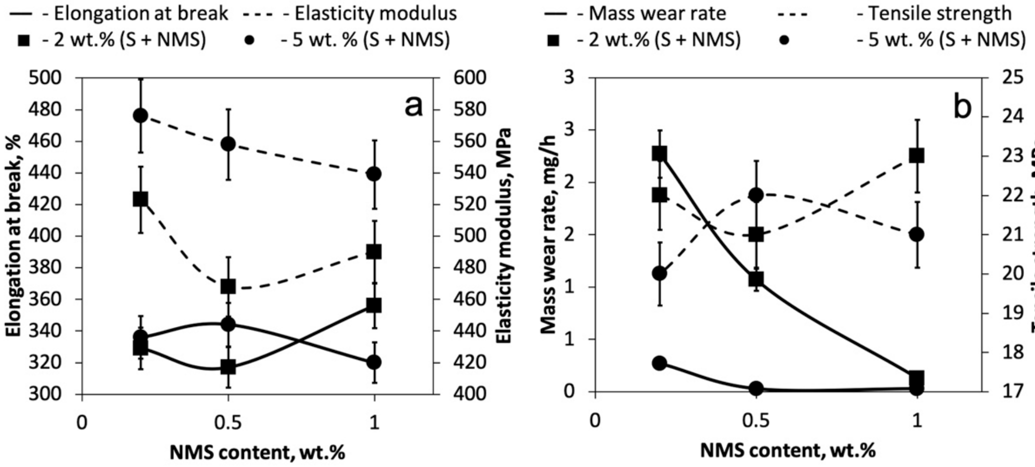

Fig. 4. The effect of the concentration of magnesium spinel on the properties of the composite

Characteristics of the composites comprising serpentinite and NMS (Fig. 4), mainly depends on the ratio of these modifiers. The relatively high NMS content leads to an increase in the tensile strength, while an increase in the silicate content in the range of 5 wt.% increases the wear resistance of the material (Fig. 4, b).

The use of layered silicates together with NMS as modifiers of the polymeric matrix contributes to a significant improvement of the tribological characteristics of PTFE: the notable decrease in mass wear rate to 2500 times in comparison with the initial polymer, which composites are characterised by a lower value of friction coefficient. One of the possible factors in the enhancement of these materials wear resistance can be an increase in the adhesive interaction of the components in the composite due to the active participation of magnesium nano-spinel in the formation of the boundary layer at the "polymer-serpentinite" interface.

Researchers in [17, 18] showed that during the process of mechanical activation of layered silicates, the Si-O-Me bonds in the octahedral layer are predominantly disrupted while maintaining the oxygen-silicon bonds in the tetrahedral layer. In the IR spectra of activated serpentinite, we detected changes in the band of stretching vibrations of the Si – O bond (Fig. 5), indicating the force changes of tetrahedral layers, which could be caused by the violation or destruction of the octahedral layer of serpentinite by mechanical energy.

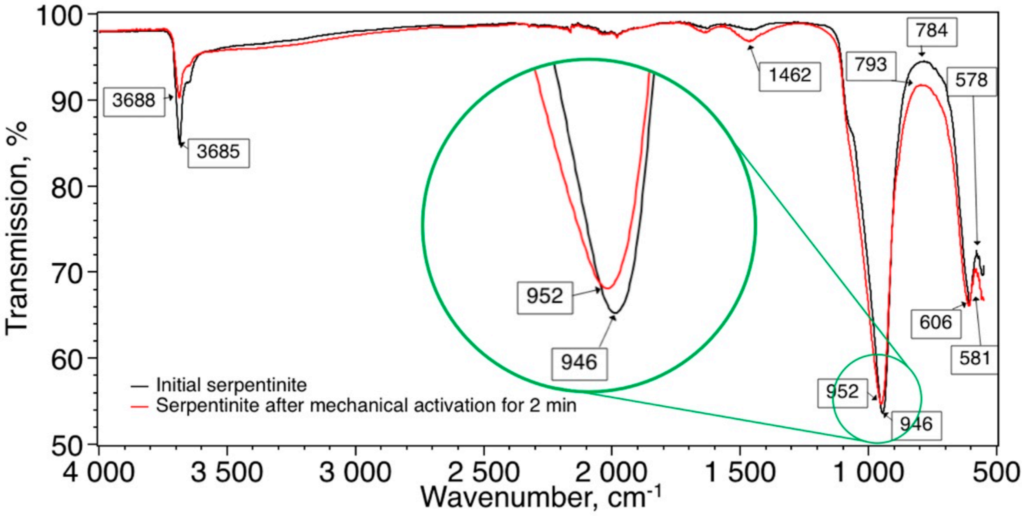

Fig. 5. IR spectra of serpentinite before and after mechanical activation

Besides, the processing of serpentinite in a planetary mill is accompanied by a change in cation exchange capacity (Table 1). The increase in CEC is most likely due to the release of magnesium — the central cation of the octahedral layer of serpentinite, as a result of its destruction.

Table 1. Cation exchange capacity of serpentinite before and after mechanical activation

Specimen	**CEC, mg·eq./100 g**
Initial serpentinite	0.3
Serpentinite after mechanical activation	2.5

In order to clarify the role of NMS in increasing the strength characteristics of the composites, we considered its structure. The structure of NMS is close to the densest cubic packing of oxygen, the tetrahedral voids of one are occupied by Mg^{2+} ions (radius 0.078 nm), the octahedral voids - $A1^{3+}$ ions (radius 0.057 nm) [16]. Thus, the introduction of NMS introduces additional magnesium and aluminium ions into the composite mixture. As known, the chemical activity of magnesium is more pronounced than that of aluminium, however, aluminium has a greater ability to form complex compounds. Besides, the ability of aluminium to bind fluorine atoms is widely used in practice [19, 20]. Complexation is based on the ability of atoms to form coordination bonds by the donor-acceptor mechanism. It appears that aluminium cations with a free orbital act as acceptors to fluorine atoms of PTFE having three pairs of electrons from one side, and to an oxygen atom with two pairs of electrons on the surface of serpentinite on the other side. Indirect evidence of such exposure are the results of XRD.

Fig. 6 shows the XRD patterns of initial serpentinite and composites with different contents of serpentinite and NMS. As seen from the XRD data, the peak corresponding to the basal reflex of the original silicate layers (curve 1) characterising periodicity manifests itself in a composite containing 5 wt.% of serpentinite ($2\Theta \approx 12$ °). In the XRD patterns of PTFE samples containing serpentinite and NMS (curves 4 and 5), this peak is not observed. The disappearance of the basal reflex indicates complete exfoliation of particles on serpentinite monolayers as a result of the intercalation of the polymer macromolecules in the interlayer space silicate (exfoliated nanostructure formation) [1]. It is observed that the peak of the original silicate on the curve 6 is shifted toward low angles, indicating an increase in the interplanar spacing silicate in the nanocomposite structure, but with the preservation of the ordered layered structure of serpentinite particles (intercalated nanostructure formation) [1, 10].

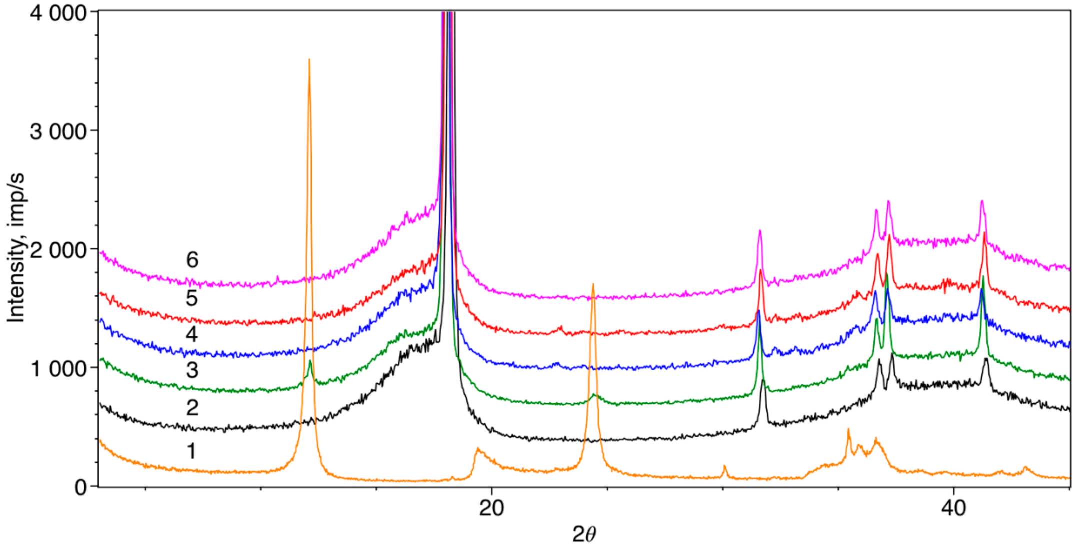

Fig. 6. XRD patterns: 1) serpentinite, processed in a planetary-type mill; 2) the original PTFE; 3) PTFE containing 5 wt. % serpentinite; 4) PTFE containing 4.8 wt. % serpentinite and 0.2 wt. % NS; 5) PTFE

containing 4.5 wt. % serpentinite and 0.5 wt. % NMS; 6) PTFE containing 4 wt. % serpentinite and 1 wt. % NMS

So, the disappearance of the basal reflex indicates that in the composites there are regions with single plates of serpentinite. In other words, the preliminary mechanical activation of serpentinite with its subsequent modification with NMS when introduced into PTFE made it possible to obtain a composite with an exfoliated nanostructure.

It is obvious the additional introduction of NMS helped to preserve these single plates in the volume of the composite compensating for the broken bonds by forming new coordination bonds with the aluminium cation.

The study of the supramolecular structure of composites formed in the field of influence of mechanically activated particles of serpentinite, using the SEM method, makes it possible to reveal their features. It is known that the introduction of highly dispersed fillers in PTFE leads to the formation of spherulitic structure. It should be noted that fairly regular spherulites are formed in the case of small concentrations of layered silicates. Due to the low density, layered silicates occupy a significant volume in the PTFE matrix even at 2 wt.%. Therefore, the structure of composites most often consists of spherulite-like formations of irregular shape.

As a rule, filler particles or areas surrounding them are zones of relative "weakness" of materials or zones of high concentration of stress. Since the destruction follows the path that requires the least expenditure of energy, an analysis of the topography of the low-temperature brittle fracture of composites can provide additional information to explain the formation of PCM.

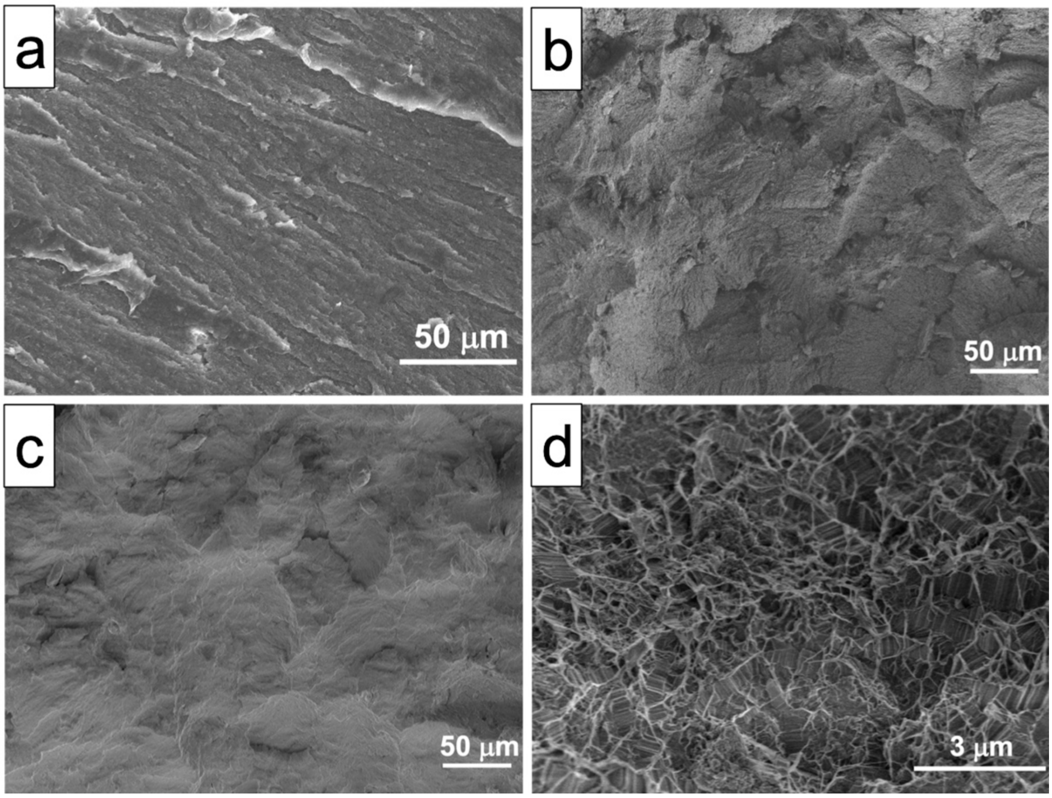

Fig. 7. SEM micrographs of the supramolecular structure of the specimens: a) initial PTFE (x 500); b) PTFE + 2 wt.% serpentinite (x300); c) PTFE + 2 wt.% serpentinite + 0.5 wt.% NMS (x 300); d) the same composite (x100000).

The analysis of the supramolecular structure of the composites makes it possible to reveal the following features: 1) the supramolecular structure of the initial PTFE changes radically - the structure of the composites is represented by spherulite-like formations instead of the characteristic lamellar structure of initial PTFE; 2) in the case of a composite containing serpentinite without magnesium spinel, the plane of destruction tends to pass from one silicate particle to another in the material (Fig. 7, b); 3) in the composite, containing magnesium spinel, there are areas in which destruction occurs along the boundaries of the defective areas of the spherulites (Fig.7, c); 4) in the magnified micrograph (Fig. 7, d), it can be seen that the silicate particles are dotted with small particles and are wrapped in the fibrils of PTFE macromolecules.

Thus, the study of the supramolecular structure of the composites proves the assumption that NMS is specific compatibilizer which enhances interactions between serpentinite and PTFE.

4. Conclusions

Developed new composite materials are characterised by high wear resistance. The effectiveness of the use of the complex modification of PTFE for the development of tribological materials has been shown: the simultaneous introduction of mechanically activated serpentinite and NMS into PTFE significantly increases the wear resistance of the material (up to 2500 times) while maintaining high values of mechanical characteristics. It is shown the increase in the mechanical strength of materials is explained by the improvement of the adhesive interaction at the interface, due to the additional introduction of NMS. It is assumed that the compatibilization ability of NMS is based on the complexing activity of the aluminium atom in its composition.

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Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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