PTFE-nanocomposites structure and wear-resistance changing in various methods of structural modification

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Abstract. Conditions of polymer materials usage containing nanoelements as modifiers significantly affect the requirements for their physic-mechanical and tribological properties. However, the mechanisms of nanoparticles effect to the polymers tribotechnical properties have not been studied enough. The article aim is to analyze the results of studying polytetrafluoroethylene modified with cryptocrystalline graphite and silicon dioxide and to determine the effectiveness of the modification methods used and methods for further improving filled PTFE mechanical and tribotechnical properties. The effect of modifiers to PCM supramolecular structure was analyzed with SEM methods. The results of modifying the PCM samples surface by depositing a copper film with ion-vacuum deposition methods and changing the structural-phase composition and tribological characteristics are considered. The findings make possible to characterize the physicochemical processes under frictional interaction in metal polymer tribosystems.

1. Introduction

Theoretical and experimental results of the researches connected to the effect of metal-polymer tribosystems modifying polymer materials to the tribotechnical properties of polymer composites have shown that the problem of predicting tribotechnical properties of multicomponent polymer composite materials is still actual [1,2]. Modifications are subject to both as separate components of the mixture as finished composite materials by changing the surface layer structure and properties [3-8]. The comparative analysis of seven PTFE-based composites presented in [4] shows that it is possible to improve PTFE properties, even if the most attractive characteristic of low friction is lost due to the presence of solid micro- and nanoparticles in the polymer matrix. The introduction of both as soft as solid phases into the polymer matrix improves its self-lubricating and supporting properties increasing PTFE tribological properties. In particular, the PTFE nanocomposite film wear resistance was increased with nanodiamonds addition [2]. All this shows that even small additions of nanofillers can change polymers mechanical and tribotechnical properties radically. The same time mechanism peculiarities of nanoparticles effect to polymers and polymer composites frictional properties had been studied insufficiently. Therefore, the task of selecting fillers type and number is being solved mostly experimentally now [2,4,6].

To optimize the structure and characteristics of material operational properties the modes of PCM sample sintering (heat treatment) technological process are changed. PCM properties are established to be significantly improved, for example, by imposing compression pressure to the sample during sintering process. One method of the surface modification is a method of thin films deposition. Work [8] studied, for example, the molecular organization of polytetrafluoroethylene (PTFE) thin coatings with included Ag, Cu and Mo nanoparticles, they are deposited from an active gas component. Due to its unique physical and mechanical properties PTFE remains one of the leading non-metallic materials used in mechanical engineering and instrument making. As a result of PTFE modification with different types of fillers it is possible to change its properties in a wide range. Thus, the analysis of metal-polymer tribosystems materials properties shows the relevance of studies according to the proved choice of
modifiers and a PTFE modifying method depending on the planned operating conditions for the metal-polymer tribosystem.

2. Statement of the problem
The basic method of PTFE structural modification and PCM synthesis is introduction fillers - modifiers of various kinds into a polymer matrix. The choice of the investigated samples component composition in this work was made on the basis of the tests presented in [6].

To conduct research the samples containing polytetrafluoroethylene (PTFE)-89 % wt, cryptocrystalline graphite (SCG)-8 % wt, dioxide silicon (white carbon black WCB-120)-3 % wt were made. The samples were manufactured in two different technologies. The first technology is a free sintering, the second technology is sintering of clips with limitation of thermal expansion in the heat treatment process.

Manufactured with various methods the samples were tested for friction and wear, when contact pressure and sliding velocity were variation factors. Samples that passed the test on the friction machine are further modified by applying a copper film, by an ion-vacuum deposition method.

The following tasks were set in this work:
1. Using methods of electron microscopy to determine the regularities of modifier or filler influence for different types and concentration and interaction modes on the structural-phase transformations in the sample.
2. To investigate the changes of PCM structural-phase state and tribological properties parameters in the case of modifying the samples surface using ion-vacuum deposition

3. Experimental results
Wear rate dependences of the nanocomposite studied (PTFE-89% wt, SCG-8% wt, WCB-3% wt) on load parameters were obtained on a universal friction machine "UMT-2168" according to the "finger-disk" friction scheme. Contact pressure and sliding velocity were adopted as variable loading parameters. Wear rate dependences graphs of the samples on the contact pressure and sliding velocity are shown in Figure 1 and Figure 2. The contact pressure varied from 1.0 MPa to 3.0 MPa with a step 0.5 MPa, the sliding velocity is 1.2 m/sec to 2.4 m/sec with an interval 0.3 m/sec.

![Figure 1](image1.png)  
**Figure 1.** The sample wear rate dependence on contact pressure at sliding velocity: 1 - 1.2 m/sec, 2-1.8 m/sec, 3-2.4 m/sec.

![Figure 2](image2.png)  
**Figure 2.** The sample wear rate dependence on the sliding velocity at contact pressure values: 1 - 1MPa, 2-2MPa, 3-3MPa.

To study physicochemical processes developing in the PCM surface layer under conditions of frictional interaction and their effect on the PCM wear resistance, the friction surface elemental composition was studied before and after friction interaction with an energy-dispersive microanalysis using JEOL JSM-5700 scanning electron microscope attachment. The results of the study are given in Table 1.
Table 1. PCM containing components, % wt

| PTFE-89wt%, SCG-8wt%, WCB-3wt% | F  | C  | O  | Si  | Ni  | Al  |
|---------------------------------|----|----|----|-----|-----|-----|
| before interaction              | 60.60 | 24.35 | 10.02 | 3.84 | -   | 1.19 |
| after interaction               | 20.29 | 51.33 | 15.44 | -   | 7.42 | -   |

A friction surface topography micrograph and simulation of the surface profile for the analysis of PCM height field samples (Figure 3) were obtained using atomic force microscopy (NTEGRA microscope).

Figure 3. Micrograph of the friction surface topography and simulation of the surface profile containing: PTFE-89wt%, SCG-8wt%, WCB-3wt%.

To modify the PCM surface and to continue the obtained samples structural-phase studies the polymer samples manufactured with technology of sintering in the terminals and containing PTFE-89% wt, SCG-8% wt, WCB-3% wt were selected. A part of the samples was previously subjected to frictional interaction of the friction machine "UMT -2168" according to the friction "finger-disk" scheme with contact pressure values 2.66 MPa and the sliding velocity 1.2 m/sec., during 90 minutes.

Figure 4. Microphotographs of the PCM surface: a) - the surface of the cold chip; b) - surface modified with copper ion-vacuum deposition.

Deposition of copper films with thickness 1 μm was produced with ADVAVAC unit on the PCM samples subjected to frictional interaction. The substrate heating was carried out at temperature 50°C. The structure of the modified ion-vacuum coating on the PCM surface and cold chip inner surface, i.e. in the sample volume (Figure 4) was investigated with electron microscopy.
To study the effect of the compressive statistical load on changes in the surface layer of a polymer sample and strength of a sputtered copper film, a different force effect was exerted on a part of the samples during 10 sec in the form of a load 98N and 294N, it was developed with a tip in the form of a pyramid used in the Vickers method. When 98N load was applied to the surface of the sample, a pyramid print was characteristic for this method, while under 294 N load, a gap in the sputtered copper film was observed. To analyze the structural-phase changes and the elemental composition with this kind of external loading, 10 sections were analyzed on three samples subjected to various force levels. The average values of elements mass fractions determined in the course of JEOL JSM-5700 scanning electron microscope are shown in Table 2.

Table 2. Content of elements in PCM with copper film surface, % wt

| Force P, Н | F  | C   | O  | Si | Fe | Cu  |
|------------|----|-----|----|----|----|-----|
| 98         | 57,25 | 32,89 | -  | 1,66 | -  | 7,20 |
| 294        | 43,75 | 23,23 | 15,61 | 1,61 | 9,27 | 6,70 |

Tribotechnical properties research of a nanocomposite modified with copper ions was carried out on a universal friction machine "UMT -2168". The obtained results in comparison with unmodified samples are given in Table 3.

Table 3. Characteristics of nanocomposites samples tribotechnical properties

| Sample composition, % | Coefficient of friction, μ | Wear rate, J,10^-4 g / h |
|-----------------------|---------------------------|--------------------------|
| PTFE-89% wt, SCG-8% wt, WCB-3% wt | 0,092 | 3,80 |
| PTFE-89% wt, SCG-8% wt, WCB-3% wt with copper ion-vacuum deposition. | 0,12 | 1,46 |

4. Discussion of the results

The results showed that when PTFE is introduced with complex and polydisperse nanosized modifiers including alongside JCG nano powder SiO₂ brand WCB-120, there is a significant change in the morphology of the polymer matrix similar to the one shown in [2,8]. In the process of friction interaction, there is a significant change in the concentration of elements decreases the fluorine content in 3 times, the carbon content is increased more than two times and oxygen is increased in half.

Analysis of the elemental composition and friction surfaces profile allows concluding that chemical and diffusion processes caused with temperature gradient in the friction zone due to frictional interaction develop on the friction surface and in thin surface layers. Under the temperature gradient effect, structural-phase changes are in the transfer film formed during the frictional interaction and in the polymer sample surface layer (i.e., where the temperature gradient is maximum) affecting the surface topology.

It follows from Figure 1 that with an increase in the contact pressure from 1MPa to 2MPa, an increase in the wear rate at all sliding velocities on average by 30% is observed, with a further increase in the contact pressure to 3MPa, a considerable increase in the wear rate is observed, 2-2.2 times compared with the wear rate at the initial value of the contact pressure.

The maximum increase in the wear rate (see Figure 2) is typical for the contact pressure 3MPa, the change in the sliding velocity is characterized with a uniform change in the wear rate for all the considered contact pressure values.

The increase in the load and, as a consequence, substantial deformation of the PCM surface layer and the copper coating applied to the samples, makes possible to determine the presence of iron and oxygen in the contact zone of the PCM sample surface and the copper film, characteristic of the transfer film.
appeared during the frictional interaction and thus forms an intermediate layer between the test sample and the sprayed coating. With an increase in the load acting on the samples under study, a substantial change in the elemental composition is observed: a decrease in the fluorine content by 20% and carbon by 30%. At the same time, the content of silicon and copper will change insignificantly in the samples.

In this case the cold chip surface is characteristic for PTFE modified with dispersed nano-modifier WCB-120 (Figure 4). It is a loosely packed lamellar structure of a polymer containing micropores. The PCM surface modified with ion-vacuum deposition has a denser structure, and it indicates that copper ions have filled the defective parts of the surface. The difference in structure is reflected in the PCM tribotechnical characteristics values. A small increase in the friction coefficient and a significant decrease in the wear rate (Table 3) are established in comparison with a similar sample without ion-vacuum deposition. Change in the friction coefficient is within the experimental error, the wear rate decreases in 2.6 times.

5. Conclusions
The PCM synthesis theory, as it considers variety and complexity of the processes occurring with materials both during the synthesis of a polymer composite and a process of frictional interaction, is not fully developed now. The fillers choice and modification of polymers with various methods makes possible to change radically properties of synthesized materials and expand significantly their application field.

As a result of the conducted studies, the following is established:
1. Analysis of changes in the chemical composition and PCM samples surface micro profile indicates the development of complex physic-chemical processes in the PCM frictional interaction conditions with a metal counter body.
2. PCM wear rate dependence on the contact pressure is non-linear, regardless of the sliding velocity and fillers concentration.
3. PCM surface modification with applying of a thin copper film by an ion-vacuum deposition method is accompanied with changes in the structural-phase state of the surface layer, it provides an increase in PTFE nanocomposites wear resistance by 2.5 times

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