The effect of ultrasonic activation on the formation of polytetrafluoroethylene modified by detonation nanodiamonds

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Abstract. The article discusses the influence of low-frequency ultrasonic vibrations on the structure and tribological properties of the synthesized polymer composite material based on polytetrafluoroethylene, modified by detonation nanodiamonds. As a result of research it is established that the effect of low frequency ultrasonic vibrations and entered a modifier of detonating nanodiamonds leads to changes the supramolecular structure of the polymer composite, expressed in the increasing the blocks size and degree of crystallinity. Studies of the elemental composition and chemical state of the atoms indicate the improvement of the composite structure, which has a better structure and contains no defects as a C-H, C-C and C-CF₃ ties and contains mainly of the –CF₂ and –CF₃ chemical bonders. Detonation nanodiamonds are introduced in the process of forming material, prevent the formation of unwanted C-H, C-C due to the absorption of excess carbon, whereby the surface of the composite material has a more perfect structure. Low frequency ultrasonic vibrations lead to the improvement of wear resistance by 13.6% and to reduce the coefficient of sliding friction is 15% of the studied composite material.

1. Introduction
High reliability of various equipment and machinery in the process of operation and also long period of its work depends on the wear of friction units. Providing a long period the work non-lubricated metal-polymer friction pairs, which are widely used in process equipment and various installations petrochemical production, directly connected to the introduction of new composite materials that have certain a preordained physical and mechanical properties [1-3]. The production of such polymer composite materials sealing devices, bearings and sliding bearings can significantly to increase the resource of work of the aggregates as a whole [4, 5].

From this point of view, the most preferable physical and mechanical properties possess the polytetrafluoroethylene (PTFE). Physico-mechanical properties of PTFE allow it to be used as the polymer matrix of the future composite. Currently there are high demands of metal-polymer friction pairs, according to their operational reliability and durability. These increasing demands stimulate the development of new composite materials based on PTFE with predetermined mechanical properties [6, 7].

The production of new composite materials with improved mechanical and tribological properties is possible by introducing in the polymer matrix the nanosized modifiers of various kinds, and also by improving the sintering process and heat treatment. However, this task can more effectively be solved through the application of new technological methods of pressing, with the simultaneous physical modification.
In the powder metallurgy, it is widely spread this method of physical modifing, as a periodic deformation (vibration or ultrasonic treatment). The most promising method of obtaining new composite materials with polymeric matrix is pressed with simultaneous imposition of low-frequency ultrasonic vibrations on the processed material.

Influence of low-frequency ultrasonic vibrations on the structure and properties of PTFE modified by detonation nanodiamonds is still poorly understood, and research in the field of materials science are very important [8-11].

2. Problem statement
The aim of this work is determination the peculiarities of the influence of low-frequency ultrasonic vibrations on the structure of the synthesized polymer composite material based on polytetrafluoroethylene modified by detonation nanodiamonds, and its tribotechnical properties.

3. Theory
The object of research is polytetrafluoroethylene (PTFE) and dispersionnoy polytetrafluoroethylene, modified by detonation nanodiamonds in an amount of 0.5 wt. %.

Samples for testing were obtained by cold pressing. Powdered polytetrafluoroethylene with a filler in the form of detonation nanodiamonds by dispersity of 4 – 6 nm, was mixed in the mill with a frequency of rotation of the knives 7800 min⁻¹, until a homogeneous composition.

The samples were produced on a specially developed installation for ultrasonic pressing on the base of a hydraulic press [12]. The installation of the ultrasonic pressing, allows the production samples with two different parameters of the pressing – as with processing of composite mixture low-frequency ultrasonic vibrations, so without the influence of ultrasonic vibrations (regime of cold pressing). Pressed samples were subjected to the same thermal treatment (sintering) the sintering temperature of 360 °C.

The supramolecular structure of the samples the composite material were investigated with using x-ray phase analysis on the device D8 Advance (Bruker), and also was used a detector Lynxeye.

For decrypt the obtained diffractogram were used ICDD database PDF-2, 2016 year in the program EVA (Bruker).

For studying the elemental composition and chemical state of atoms in the studied samples of the fluoropolymer modified by detonation nanodiamonds have been applied a highly sensitive method rentgenospektralny spectroscopy (XPS), implemented analytical complex LAS-3000 (Riber). For creating x-ray radiation was applied to the source with anode of aluminum and a voltage on the anode of 1487 eV. XPS spectra were recorded at a pressure of ~10⁻⁹ Torr in the analyzer MAS-2. The x-ray beam was applied from a power source by nominal power of 240 W, the beam diameter was ~5mm.

A study of the tribological properties the samples obtained polymeric composite material was carried out on the stand MDS – 2 [13].

4. Results of experiments and its discussion
Studies of composite materials were carried out by studying the supramolecular structure and phase composition of the obtained materials by the method of x-ray phase analysis (RFA). Analyzing X-ray diffractograms, may be to obtain information about the molecular structure of the composite.

Deciphering the phase composition of the PTFE sample showed that it is a homogeneous object in which PTFE phases are present (Figure 1).
Figure 1. Phase composition of the sample PTFE.

On the diffractogram of PTFE there is a powerful peak at d/n = 4.90 Å (18.01° 2θ) and a number of peaks the small intensity. Along with this, in the region of 30 – 50° (2θ) two amorphous halos. The appearance of an amorphous halo in the diffractogramm the phase composition of PTFE speaks that random macromolecules have certain forms which are different from the amorphous and crystalline phases of other polymers.

Figures 2 and 3 shows a diffractogram the samples of composite material modified by detonation nanodiamonds. A diffractogram consists of reflexes: a powerful reflex of the crystalline phase in the region of 18°; a set of narrow peaks at 36 – 40°; pronounced amorphous halo with 30 – 42° (Fig. 2,3).

Figure 2. Phase composition of the sample without ultrasound.

Figure 3. Phase composition of the sample without ultrasound.
It should be noted that the main reflex of the fluoropolymer (at 18 °) is split into two lines, which can indicate the presence of phases with different arrangements of macromolecular fluorocarbon chains. The ratio of squares the interplanar spacings of the first, second and third crystalline reflexes shows that the composite material has a hexagonal crystal cell. Radiograph of the samples subjected by ultrasonic effect differ from diffractogram the samples of fluoroplastic the absence of reflexes [14].

Decoding of the phase composition of the samples showed that on the X-ray pattern of the samples with DNA contains only peaks related to PTFE. Reflexes characteristic for the DNA phase were not detected. Apparently, this fact is related that the DNA has a small size of the primary particles, 4-4.5 nm that leads to a significant broadening of the diffraction maxima, in addition the most intense peak the phase of the DNA overlaps with peaks from the phase of PTFE. All this leads to the fact that the total picture dispersion of clear peaks from the phase of DNA on the radiographs samples is not observed. Another possible explanation of this fact may be a low content the phase of DNA in the researched samples.

For samples of the studied composites was carried out additional processing of the received radiograph in order to extract information about the characteristics of their supramolecular structure.

For determining the position of diffraction maxima and the area under the peaks was used the program Fityk. The background was subtracted linearly in the range of angles θ: 9-25°. To describe the profiles of the peaks function was used PseudoVoight.

Estimated parameters of the permanent crystal hexagonal cells of $a_{kr}$ and $c_{kr}$, and the degree of crystallinity of the investigated samples of composite material are presented in table 1.

| Marking of the sample | SK,% | $a_{kr}$ nm | $c_{kr}$ nm | $D$, nm |
|-----------------------|------|-------------|-------------|--------|
| Without ultrasound    | 40   | 0.5693      | 1.588       | 33.4   |
| With ultrasound       | 46   | 0.5681      | 1.579       | 38.5   |

A diffractogram of the researched samples, independently the mode of pressing, reflect amorphous-crystalline structure the mixture of DNA and PTFE with a high degree of crystallinity (40-46 %). In this case the diffraction reflections the crystalline part of the polymers are at constant angles of 2θ, that indicates about the invariance of the phase composition during ultrasonic treatment.

At the same time, the constant crystal hexagonal cells of $a_{kr}$ and $c_{kr}$ reduced as a result of processing PKM by ultrasound, and the size of crystallite in the direction [100] increases. The degree of crystallinity substantially increases to 16 %.

Thus, the joint effect of ultrasonic treatment and particles of the filler leads to significant changes the morphology of the PTFE. There is a change of degree the crystallinity and morphology of polymer (formed crystal structures of two different types).

Figure 4 shows the overview XPS spectra of original and modified fluoropolymers. In both spectra, the observed lines of the carbon C 1s (∼290 eV), lines of fluorine F KVV (∼840 eV), F 1s (∼690 eV), F 2s (∼31 eV) and lack lines of other elements. Analysis of overview spectra showed that in the case of the initial sample a line of the carbon C 1s has two local maximum, that indicates on a different chemical environment of the carbon in the samples.

Quantitative analysis performed on the most intense lines of the elements showed that in the surface layer of the modified sample tend occur higher fluorine content compared to the original fluoropolymer (table 2).
Table 2. Quantitative analysis of samples by method XPS.

| The sample       | Concentration, at.% | [F]/[C] |
|------------------|---------------------|---------|
|                  | F       | C       |         |
| Without ultrasound | 64.2    | 36.1    | 1.77    |
| With ultrasound  | 71.2    | 28.8    | 2.47    |

Figure 4. Overview XPS of the sample without ultrasound (1) and with ultrasound (2).

Figure 5 shows the lines of C 1s carbon for both samples. In the spectrum of the original fluoropolymer, the maximum on the binding energy of ~285 eV responds to the superposition of states a carbon as part of C-H, C-C and C-CF\textsubscript{n} bonds. The high-energy maximum at ~293 eV corresponds to carbon essentially composed –CF\textsubscript{2} bonds [15-17].

Figure 5. XPS C 1s spectra of the sample without ultrasound (1) and with ultrasound (2).

The existence of maximum on energy of ~285 eV indicates on the imperfection of the structure the original fluoropolymer, that is most likely due to with the formation of C-C and C-H chemical bonds in the process of obtaining this material. The ratio concentration of fluorine to carbon (Table 2), which for this sample amount 1.77, also indicates on the imperfection of the fluoropolymer structure due to the presence of C-CF\textsubscript{n} chains (n<2) [15-17]. In the spectrum of a modified fluoropolymer
manufactured with using of ultrasonic vibrations, an intense high-energy maximum of the C 1s line is observed at energies ~ 293 eV, and there are practically no states at the binding energy ~ 285 eV. This indicates on a better structure of the modified fluoropolymer containing a lower amount of C-C, C-H. In addition, the ratio concentration of fluorine to carbon (Table 2) for this sample amount ~ 2.5, that may says an increase in the proportion of carbon atoms in the chemical –CF₃ bonds.

Figure 6 shows the F 1s fluorine lines for both samples. In the spectrum of the starting fluoropolymer, the maximum on the binding energy amount ~ 690 eV corresponds to the superposition of fluorine states in the –CF₃ and –CF₂ bonds [14–16]. In the spectrum of the sample manufactured according to the standard technology there is a low-energy shoulder, that confirms the presence of defect states in polymer structure. In the spectrum of the modified fluoropolymer is observed shift of the maximum of the F 1s line towards high binding energy, that may be associated with the increase in the proportion of –CF₃ bonds.

![Figure 6. Overview XPS spectra of the sample without ultrasound (1) and with ultrasound (2).](image)

Conducted XPS analysis showed that the polymer composite material manufactured without activating by ultrasonic vibrations contains defects in the form of C-H, C-C, which lead to the formation of a defective C-CF₆ bonds. Surface layer of the sample manufactured with ultrasonic activation has a better structure and does not contain defects in the form of C-H, C-C and C-CF₆ ties and consists primarily of the –CF₂ and –CF₃ chemical bond. Detonation nanodiamonds are introduced in the process of forming material, prevent the formation of unwanted C-H, C-C due to the absorption of excess carbon, whereby the surface of the fluoropolymer has a more perfect structure.

The study of tribotechnical properties the samples obtained polymer composite material showed that the introduction of low-frequency ultrasonic vibrations in the pressed material to an increase in wear resistance by 13.6%. Along with this, the effect of low-frequency ultrasonic vibrations leads to a decrease in the coefficient of sliding friction by 15% of the composite material under investigation.

5. Findings and conclusion

As a result of researches it is established that the effect of low frequency ultrasonic vibrations and entered a modifier of detonating nanodiamonds leads to changes the supramolecular structure of the polymer composite, expressed in the increasing the blocks size and degree of crystallinity.

Studies of the elemental composition and chemical state of the atoms indicate the improvement of the composite structure, which has a better structure and contains no defects as a C-H, C-C and C-CF₆ ties and contains mainly of the –CF₂ and –CF₃ chemical bonders. Detonation nanodiamonds are introduced in the process of forming material, prevent the formation of unwanted C-H, C-C due to the
absorption of excess carbon, whereby the surface of the composite material has a more perfect structure.

Low frequency ultrasonic vibrations lead to the improvement of wear resistance by 13.6% and to reduce the coefficient of sliding friction is 15% of the studied composite material.

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