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MODIFICATION OF POLYTETRAFLUOROETHYLENE ON THE BASE OF ULTRAFINE POWDER

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This paper presents the results of a study of the influence of thermal and mechanical effects on the formation of a structure in an ultrafine powder heated to a temperature above the melting point of polytetrafluoroethylene (327°C). The ultrafine powder was obtained by mechanical grinding of an industrial sample of polytetrafluoroethylene in a rotary knife mill. Studies of the ultra powder with a transmission microscope showed that the powder particles are quasi-spherical particles of a size of 5 microns. The thermal (sintering, slow and fast quenching) and mechanical (creation of high pressure) effects on ultrafine powder particles were determined by the methods of an automated digital microscope Leica DM 6000, X-ray diffraction, and Vickers. It was found that the formation of a supramolecular structure depends on the applied force (pressure) and temperature. Measurement of the hardness of the modified sample showed that its hardness in relation to the hardness of the industrial sample increased by 4 units.

Keywords: *polytetrafluoroethylene, modification, ultrafine powder, supramolecular structure, thermal and mechanical effects*

Introduction

With the growing requirements for polymers, the problem arises from finding alternative ways to improve the properties of polytetrafluoroethylene (PTFE). Despite the comprehensive list of known positive qualities and properties, PTFE has several technological disadvantages that restrain the active use of this material. We can say that modern technologies of fluoropolymers have exhausted their innovative potential, and there is a search for new forms of fluoropolymers, technological methods that eliminate the noted limitations. Proceeding from this, to eliminate the noted limitations and more efficient and expanded application of PTFE, the problem arises of the need to modify it in various ways and to find new ways to improve its properties. Over the years, many approaches [1-11] have been developed for modifying PTFE to improve certain properties. The main ones include copolymerization. Such traditional approaches have made it possible to achieve serious results, but today it can be stated that they have not made it possible to make a qualitative leap in improving the properties of the resulting composites. In particular, with the help of all of the above, it is not possible to overcome the limit reached for the wear rate during friction without lubrication and is $(0.5 - 1.0) \times 10^{-7}$ μm/km. The same applies to creep, hardness and radiation resistance of PTFE-based composites. Currently, the most effective method for solving this problem is: - creation of ultrafine (nanosized) PTFE powders. It is known [12] that adhesion of nanoparticles is very high. This article studies the influence of the thermal and mechanical effects on the processes of contact interaction of ultra dispersed particles.

1. Material and research methods

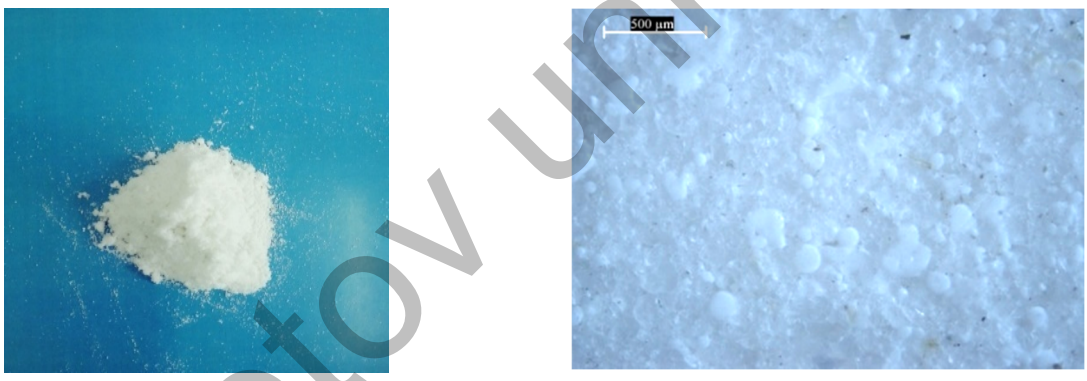
The studied object was the ultrafine powder (UPTFE) with a particle size of up to 5 μm, obtained by mechanical grinding of an industrial PTFE sample in a rotary knife mill. Ultrafine powder heated to a temperature above the melting point of PTFE (327°C). The analysis of the shape of the UPTFE powder particles and the supramolecular structure of the modified PTFE for reflection and transmission was carried out on an automated digital microscope (ACM) Leica DM 6000 M (Nanotechnological laboratory of the engineering profile, KazNU named after al-Farabi). To obtain samples from PTFE nanopowder, we applied the following technology [4]. At the preliminary stage, cylindrical samples 10 mm in diameter and 4 mm in height were formed from the powder during cold pressing on a special mechanical press.

The press was a screw with an M15 thread, which, with the help of knobs, created a force of up to 7000 Newtons. Under the screw was a mold made of steel with a diameter of 40 mm and a height of 30 mm with a

plunger with a diameter of 10 mm and an area of 0.78 cm. The surfaces of the mold and the base were made with high precision and were fastened together with two 5 mm screws, which excluded powder leakage. A dosed amount of PTFE nanopowder was poured into a mold, in which a pressure of 35 MPa was created. To create a stationary pressure on the powder, the plunger of the mold was pressed by a spring with a force of 300 Newtons. At the second stage, the mold with the sample obtained by cold pressing was placed in a SNOL muffle furnace and kept in it up to the sintering temperature T = 393^{0}C. The temperature in the muffle furnace was set automatically and the sintering time was 20 minutes per mm of thickness. Shrinkage of the sample during heat treatment was compensated by the force of the spring placed on the plunger. After sintering, the sample was removed from the mold and cooled under running cold water. X-ray diffraction data for UPTFE powder were obtained on a MiniFlex-600 bench top X-ray diffractometer (RIGAKU, Japan). Shooting conditions: voltage across the tube 40 kV, current in the tube 15 mA, anode material - copper, range of scanning angles from - 3 ° to 145 ° (depending on scanning Θ-2Θ.). The scanning speed was from 0.01 to 100 ° / min (2Θ). The minimum step is 0.005 ° (2Θ.). X-ray structural data of the modified PTFE sample were obtained on a DRON-7 diffractometer at a sintering temperature T = 393^{0}C (Nanotechnological laboratory of the engineering profile, KazNU named after al-Farabi). Shooting conditions: interval: from 10.00 ° to 100.00°, survey method: 2theta - theta, exposure, sec. = 1, shooting step, deg. = 0.050 °. The hardness of the samples was measured with Vickers's tester.

2. Results and discussion

Figure 1a shows the ultrafine UPTFE powder. Figure 1b shows a microphotograph of UPTFE powder. The transmission microscope studies of the UPTFE powder have shown that the powder particles are quasi-spherical particles with a size of 5 μm.



a) b)

Fig.1. a) Ultrafine PTFE powder, b) microphotograph of UPTFE powder.

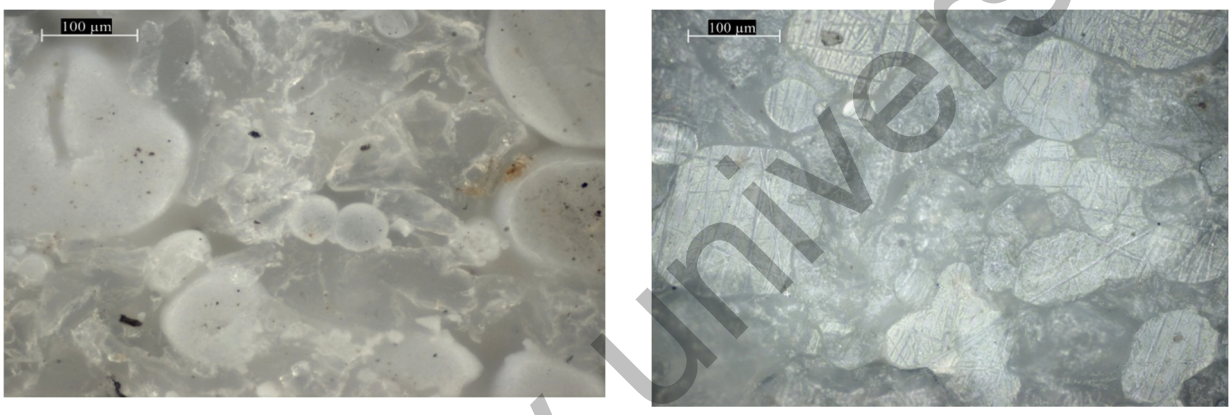
Monoparticles of UPTFE powder consist of smaller blocks combined into conglomerates, which, in turn, form associates larger than 10 μm in size. In addition to quasi-spherical formations that make up most of the elements of the powder, the blocks and the polymer filling the space between them have a different structure. As a result of this technology, we received modified samples, which are presented in Figure 2 a, b.

a) b)

Fig.2. Modified PTFE samples obtained a) cold pressing, sintering at the temperature T = 393 ^{0}C and rapid quenching; b) after sintering at the temperature T = 393 ^{0}C, slow quenching and standing under the press for a day.

The first sample (Fig.2a) obtained from PTFE powder by cold pressing and sintering at the temperature of T = 393 ° C and rapid quenching. The second sample (Fig. 2b) obtained by sintering, slow quenching and standing for a day under the press,

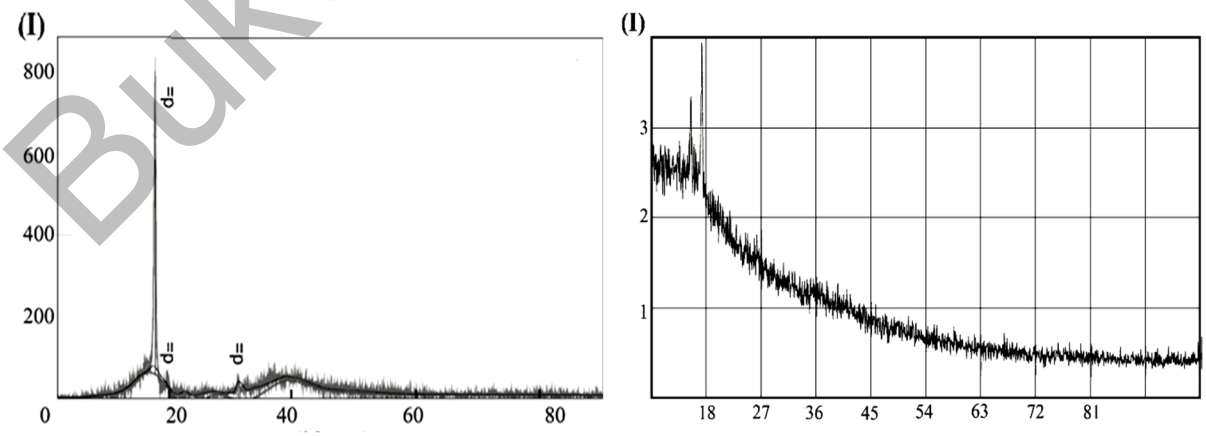
Figure 3a shows an electron microphotograph of a sample obtained from PTFE powder by cold pressing and sintering at the temperature of T = 393 ° C. In the bulk of the sample (Fig. 3a) obtained by cold pressing and sintering of PTFE nanopowder, it was found that pressing, sintering, and rapid quenching lead to a change in the morphology of the UPTFE structure. The sample contains loosely packed, separated from each other globular, extended, not having a definite shape, supramolecular formations - crystallites. However, a microphotograph of the second sample (Fig. 3b), obtained by sintering, slow quenching and standing for a day under the press, a completely different picture is observed. Here we find that the supramolecular structure is tightly packed, monotonic and uniform throughout the matrix. We observe crystalline formations in the form of bundles - lamellas, having strictly defined shapes and sharply defined boundaries. Blocks in the form of packs are tightly knit together. Gaps between blocks are not observed. These blocks are arranged in an orderly manner. Such a supramolecular structure allows us to conclude that sintering, and then the subsequent slow quenching of the sample and prolonged holding of the sample under pressure for a day, change the structure of the crystal lattice and increase the degree of crystallinity of the sample.



a) b)

Fig.3. Microphotographs of modified PTFE specimens obtained a) by cold pressing, by sintering at a temperature of T = 3930C, b) after sintering, which stood under the press for 24 hours.

This is confirmed by the data of X-ray diffraction analysis .The X-ray diffraction pattern (Fig. 4a) of the ultrafine PTFE powder shows an intense peak at an angle (2θ = 18.158 °) and an amorphous halo at an angle (2θ = 40.00).



a) b)

Fig.4. X-ray profiles of ultrafine powder (a) and modified PTFE (b).

An intense peak at an angle (2θ = 18.158 °) is a first-order phase transition II → IV and is caused by the rearrangement of the crystal lattice from triclinic II to a three-dimensional hexagonal cell IV with parameters a = 5.653 Å, c = 19.512 Å at a temperature of 20^0 C, which is characteristic of crystalline PTFE, which is in good agreement with the literature data [12]. In the X-ray diffraction pattern (Fig. 4b) of the modified PTFE, in addition to the peak at an angle (2θ = 18.158 °), a second peak is observed at an angle (2θ = 16. 396^0), which are less intense. The appearance of only two reflections of the form (h, k, l) means that this set of reflections is described by a flat (two-dimensional) hexagonal lattice with the parameter a = 5.681 Å.

The lattice parameter is in good agreement with the unit cell parameters of PTFE at a temperature of 27^0 C. The presence of only basal-type reflections in the X-ray diffraction pattern is caused by the strong preferential orientation of particles on the surface [12, 13]. The hardness values of the industrial and modified PTFE samples are presented in Table 1.

Table1. Hardness values of industrial and modified PTFE samples

Vicker's hardness, **HV**	
Industrial sample	58
Modified	62

The measurement of the hardness of the modified PTFE sample showed that its hardness in relation to the hardness of the industrial sample increased by 4 units [14].

Conclusion

1. The technology of the modification of the structure and properties of the ultrafine PTFE powder was developed using a special mechanical press and heating powder to the melting temperature of PTFE.

2. It was found that the energy activation of the ultrafine PTFE molecules and the formation of a supramolecular structure depend on a high mechanical pressure, temperature.

In the ultrafine powder, PTFE molecules are clusters of three atoms. Atoms located at the ends of the molecule come into contact and a bond is formed between the atoms. These forces are directly proportional to the contact area of the atoms. The applied force (pressure) influences on these forces through the actual contact area. When the pressed powder is heated to the melting point of PTFE, the contact between the atoms of the pressed powder becomes plastic, and the actual contact area increases significantly.

3. The practical significance of obtained research results will allow them to be used in the development of new polymer materials characterized by an improved set of operational properties.

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