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X-RAY STRUCTURAL STUDIES OF POLYETHETRAFLUOROETHYLEN

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X-ray diffraction studies of ultradisperse powder, ordered with the spiral structure of industrial (F-4) and modified polytetrafluoroethylene (PTFE) on different X-ray machines with different shooting conditions were performed. The obtained X-ray diffraction patterns are noticeably differed between themselves. In contrast to X-ray diffraction patterns of ultrafine powder, which has two reflexes and a modified PTFE with a single reflex, on the fluoroplastic-4 X-ray diffraction pattern, in addition to the polytetrafluoroethylene line, additional diffraction peaks (a wide diffuse halo and a series of reflections) that indicate the presence of several phases of fluoroplastic or a modification of the structure were found. The analysis of X-ray diffraction patterns showed that the standard PTFE line observed at an angle ($2\theta = 18.15$ °) is typical for all samples. It was established that the difference in X-ray diffraction patterns is due to the prehistory of obtaining PTFE samples.

Keywords: X-ray diffraction pattern, polytetrafluoroethylene, powder, ultra disperse, helical structure, hexagonal cell, lattice, sample, profile, crystalline object.

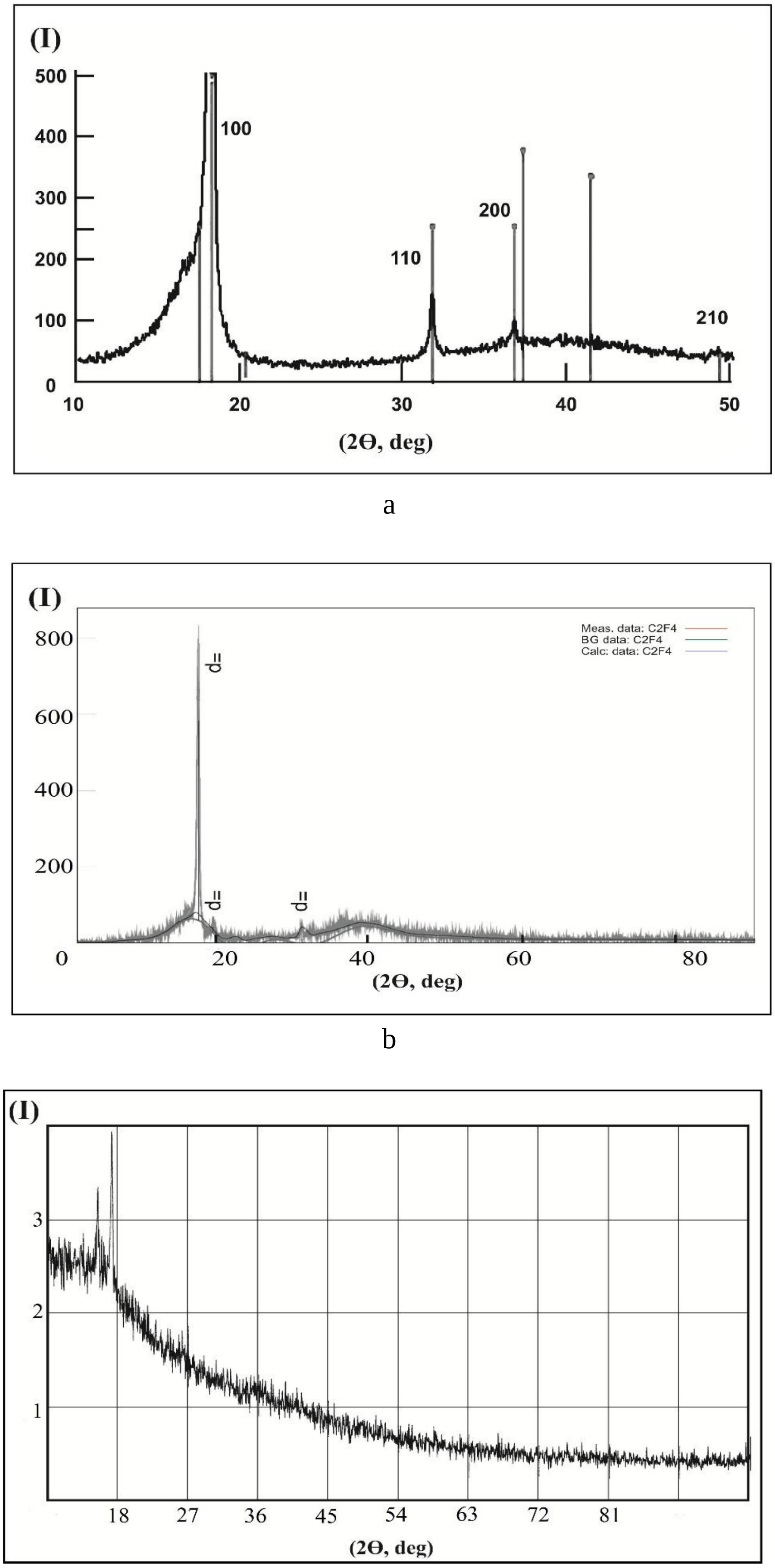
Introduction

In recent years, there has been a significant increased in interest in the radiation modification of polytetrafluoroethylene (PTFE) and composite materials based on it obtained by the action of beams of different particles, including high-energy electrons. The considerable attention to PTFE is associated with the discovery of a significant improvement in a number of important from the point of view of practical properties of this polymer after radiation exposure in the temperature region above the melting point.

The main emphasis in this case is done on molecular mechanisms and molecular structure since the macroscopic properties of PTFE depend on its supramolecular structure and morphology. In this regard, the study of the morphology of the radiative modifications of PTFE along with the elucidation of molecular mechanisms is of independent interest especially when studying the properties of compositions based on PTFE with electrically conductive fillers of complex composition, a filler made from modified carbon fiber reinforced with quartz, using ultrafine inorganic compounds like aluminum-silicon oxynitride which is a solid refractory solution with an average particle size of 100 nm, at the study of modified PTFE films and their modification [1, 2]. Proceeding from the foregoing the considerable interest represents a study of the crystalline structure of PTFE which has a high degree of crystallinity both immediately after production of the material and at the present time. The special meaning information on the crystal structure is acquired in connection with the need to clarify the nature of various modifications and derivatives of PTFE including composite and ultra disperse materials and understanding their structure.

Therefore, for the analysis and interpretation of the structural structure of various modifications and derivatives of PTFE it is necessary to carry out a comparison with the data for industrial PTFE.

In this paper, profiles of X-ray patterns of samples of ultra disperse powder of (PTFE) (a), industrial PTFE-4 (b) and modified PTFE (c) have been studied (fig.1).



a

b

c

Fig.1. X-ray profiles of ultra disperse powder (a), PTFE-4 (b) and modified PTFE (c).

1. Experimental installations and measurement techniques

In the case of UPTFE the powder diffractometry method was used. X-ray diffraction data for a sample of PTFE were obtained on a MiniFlex-600 tabletop X-ray diffractometer from RIGAKU (Japan). The 5th generation MiniFlex-600 diffractometer is a multifunctional instrument intended for high-quality and quantitative phase analysis of polycrystalline materials.

MiniFlex is the only desktop X-ray diffractometer equipped with an automatic sample loader. The sample was an ultrafine PTFE powder. Survey conditions: tube voltage was 40 kV, tube current was 15 mA, and anode material was Cu, scan angle range from – 3 ° to 145 ° (scanning dependent ϴ-2ϴ). The scanning speed was from 0.01 to 100 °/min (2ϴ). The minimum step is 0.005 ° (2ϴ.)

The X-ray diffractometer DRON-7 is a general-purpose diffractometer designed to measure the intensity and angles of diffraction of X-rays scattered by a crystalline object in solving X-ray diffraction and X-ray diffraction analysis of materials and is used in industrial, research and training works in various fields of science and production (materials science, ferrous and non-ferrous metallurgy, machine building, mineralogy, crystallography, chemistry, pharmacology, criminalistics and others). X-ray diffraction data of the modified sample were obtained by the DRON-7 diffractometer at 20 – 22 °. The operation of the diffractometer is controlled from a personal computer (PC). It is designed to work with the following factors: a) ambient temperature from 10 to 35 ° C; b) relative air humidity up to 80% at 25 ° C; c) atmospheric pressure of 84 – 107 kPa (630 – 800 mm Hg) and provides operation with X-ray tubes of the type BSV27, BSV28 and BSV29 in the third design version.

The basic set includes an X-ray tube 2.5BCB27-Cu. The measuring range of angles 2θ is from minus 100 to plus 165 °; the measuring range of the angles is from 0 to 360 °. The power of the diffractometer is provided by a single-phase alternating current network with a frequency of (50 ± 1) Hz, by the voltage of 220 V with a permissible deviation of ± 10 % from the nominal value. The power consumed by the diffractometer is not more than 5.5 kW.

The steady speed of angular movements along the axis of the bracket of the detection unit and the axis of the sample is at least 500 °/min. The absolute error in measuring the angular positions of the diffraction maxima does not exceed ± 0.02 °The basic instrumental error in measuring the counting rate of X-ray pulses does not exceed 0.25 %.

When measuring the X-ray diffraction spectrum, a diffractometer with a PC provides automatic output of information to peripheral devices. The limit of the permissible deviation of the installation of the angular position of the bracket of the detection unit and the sample holder from the specified angle of rotation is ± 0.005. The minimum scanning step is 0.001.

The diffractometer DRON-7 uses the characteristic CuK_α radiation with a wavelength λ = 1.54178 monochromatized with a monochromator crystal, the shooting step is 0.50. The scan interval is 10 – 100^o for 2θ shooting method: 2THETA-THETA. Exposure = 1 sec.

X-ray diffractometry studies of an industrial fluoroplastic sample were performed on an automatic diffractometer Bruker D8 Advance with a digital recording of the measurement results. The survey was carried out in the geometry of a divergent X-ray beam with Bragg-Brentano focusing (BB). The D8 ADVANCE automatic x-ray diffractometer (Bruker AXS GmbH, Germany) is designed for X-ray diffraction studies of various crystalline materials in scientific research institutions and laboratories of industrial enterprises. The investigated samples were a fluoroplastic film reinforced on a glass substrate and a fluoroplastic plate with a thickness h = 1.5 mm cut from the cross-section of a rod with a diameter d = 40 mm.

To record the diffraction pattern at a temperature of 15° C, the fluoroplastic plate was placed on the tantalum tape of the heater of the high-temperature vacuum chamber with the front cover removed. Measurements at a temperature of 15 and 20 ° C were carried out at atmospheric pressure, heating the sample to 50 and 60 ° C was carried out after pumping the high-temperature vacuum chamber with a turbo molecular pump to a pressure of 1. 10^{-4} mm Hg. X-ray patterns of the samples were obtained on a diffractometer using copper radiation and a graphite monochromator on a diffracted beam. The sample shooting mode was as follows: the voltage on the X-ray tube 40 kV at a current of 40 mA. The scanning step was 0.02 degrees 2θ; the diffraction intensity measurement time at this step was 5.0 seconds. The sample in the standard holder rotated in its plane at a speed of 60 t/m. A high-temperature vacuum chamber was used for shooting intensity of diffraction at a sample temperature of 50 and 60 °C.

2. Results and discussion

On Figure 1a, b and c X-ray diffraction patterns of ultra disperse powder, PTFE-4 and modified PTFE are presented. As is seen from the X-ray diffraction patterns they differ from each other. On the other hand, for all PTFE samples with a scattering angle $2\Theta = 18.158^0$ an intense peak characterizing the crystallinity of the sample is observed.

The X-ray pattern of the ultrafine PTFE powder is somewhat unusual for a crystalline substance there are two peaks one less intense ~ 16.396^0 (2θ) characterizing an amorphous halo and a disproportionately intense peak at 18.158 °. The appearance of only two reflections of the form *(h, k, 0)* means that this set of reflections (Table 1) is described by a planar (two-dimensional) hexagonal lattice with a parameter, a = 5.681 Å. The value of the lattice parameter corresponds well to the parameters of the PTFE unit cell at a temperature of 300 K [1]. The presence on the X-ray patterns of only basal type reflexes is caused by a strong predominant orientation of the particles on the surface.

Table 1. X-ray diffraction data of ultrafine PTFE powder a = 5.653 Å for a planar symmetry group

$2\theta^o$	d, Å	I, %	*h*	*k*	*l*
16.396	2.8271	100.0	1	0	0
18.040	4.9297	100.0	1	1	0

On X-ray diffraction pattern of industrial fluoroplastic-4 in contrast to ultrafine powder and modified PTFE there are a number of additional diffraction peaks and a wide flat region that can be interpreted by a phase transition II → IV from a triclinic lattice II to a three-dimensional hexagonal cell IV with parameters a = 5.653 Å, c = 19.512 Å at a temperature of 293 K which also agrees well with the literature data [3, 4].

The phase transition II → IV consists in decreasing the twist of the helix from the state 13_6 (13 segments per six complete turns of the helix) to 15_7 in terms of helical symmetry. Further transformation is considered as a loss of ordering along the packing axis of macromolecules of the polymer which is manifested in the mutual rotation of individual, adjacent spirals [1].

On the X-ray diffraction pattern of the modified PTFE only one intense reflex is observed at an angle of $2\theta = 18.00$ ° corresponding to the crystalline form II. The absence of additional reflexes can be interpreted in that when pressing the powder under high pressure then heating above the melting point and abrupt cooling leads to the formation of crystalline form II, namely, the triclinic lattice.

Conclusion

1. New experimental data on the X-ray diffraction patterns of ultradisperse powder, industrial and modified PTFE have been obtained. It is shown that the X-ray diffraction patterns are strongly differed between themselves.

2. Comparison of the X-ray diffraction patterns of ultradisperse powder and modified PTFE with an industrial X-ray diffraction pattern revealed the nature of the structure of the powder and modified of PTFE.

3. The practical significance of the obtained research results will allow them to be used in the development of polymer composite materials based on PTFE for clarifying the nature and understanding of their structure.

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REFERENCES

1 V.M. Buznik, V.M. Fomin, A.P. Alkhimov et al. *Metal polymer nanocomposites*. Novosibirsk, Publishing house of the SB RAS. 2005, 56 p. [in Russian]

2 Prierce R.H., Clark E.S., Whitney J.F., Bryant W.M.D. Crystal Structure of Polytetrafluoroethylene. *Proceeding of the 130th Meeting of the American Chemical Society,* 1956, pp. 9 – 14.

3 Clark E.S.and Muus L.T. Technology of Fluoropolymers // Z. Krist., 1962, B.117, pp. 108 – 118.

4 Clark E.S., Muus L.T. Technology of Fluoropolymers // Z. Krist., 1962, B.117, pp. 119 – 127.

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