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## Structure of Ultrafine Polytetrafluoroethylene Powders Obtained from Industrial Wastes *via* Hydrothermal Method

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### Abstract

The structure of ultrafine polytetrafluoroethylene (PTFE) powder obtained *via* waste PTFE thermal treatment by superheated steam was studied. The condensation of the resulting gaseous pyrolysis products has been performed with the use of water. The features of molecular and morphological structure of the powder have been established, the potentialities of its practical application have been revealed. The technology allows processing the wastes on the industrial scale to obtain commercial product, thus solving one of the problems of fluoropolymer production.

**Key words:** polytetrafluoroethylene, steam thermal processing, structural features

### INTRODUCTION

Polytetrafluoroethylene (PTFE) exhibiting a number of unique properties finds application in many branches [1]. At the same time, there is a number of factors limiting a wider application of PTFE, in particular, a high cost of the polymer and an abundance of waste products difficult for repeated recycling. Recently, an active search is on for the methods of industrial waste processing to obtain a useful product. So, the pyrolysis of industrial wastes resulted in obtaining the Forum trademark ultrafine PTFE powder [2] which has found an application as a resource-saving additive for motor oils. As it was demonstrated in the stud-

ies presented in [3], the powder exhibits specific molecular, supramolecular and morphological structural features different from those inherent in the samples of industrial Fluoroplast-4 (F-4, Teflon). The present work is devoted to the studies on the structure of the powder obtained by the method of continuous pyrolysis of F-4 waste products with the use of superheated water vapour [4]. It should be noted that the structure, properties, application fields of PTFE powders [3] to a considerable extent depend on the type of technology and the mode of synthesis, which determines the urgency of studies performed concerning the structure of the powders, in particular of those obtained *via* a new method.

## MATERIALS AND METHODS

The technology of waste product processing has been developed at the Polymer Plant of Kirovo-Chepetsk Chemical Combine [4]. According to the technique proposed, the polymer was loaded into a reactor as a granulated material with an average particle size ranging within 3–6 mm obtained via grinding of waste products resulted from F-4 extrusion wares, to treat by superheated steam. The temperature of pyrolysis reaction amounted to 590–610 °C, the mass ratio water vapour : polymer = 10 : 1. The quenching of pyrolyzate was performed by deaerated water injecting into the gas flow. After the separation of water condensate and gaseous pyrolysis products (mainly tetrafluoroethylene, hexafluoropropylene and octafluorocyclobutane) the separation of fine powder was carried out *via* filtering at underpressure. The sample (so-called initial) represented a humid light-beige powder which turned into a loose powder (processed sample) after heating at the temperature of 120 °C. It is obvious, that the use of water in the process of obtaining the powder should result in the fact the powder would differ in structure from the powders obtained by other methods with “softer” condensation methods. In particular, alongside with fluorocarbon macromolecules, the formation of molecular groups containing hydrogen is quite possible.

In order to perform investigations concerning the solubility of low-molecular fractions of a powder in supercritical carbon dioxide (SC-CO<sub>2</sub>) we used a static method (without flowing-through SC-CO<sub>2</sub>) employing a high pressure experimental setup described in [5].

The morphology of powder particles was studied by scanning electron microscopy (LEO-1420, Carl Zeiss, Germany). The function of particle size distribution was measured employing Fritsch Particle Sizer Analysette 22 device. The studies on thermal properties were carried out using Netsch STA 409 PC Luxx apparatus within the range of 20–600 °C with the heating rate amounting to 10 K/min. The X-ray diffraction studies were carried out on a Shimadzu XRD-6000 diffractometer at a room temperature within the range of 3–110° (2 $\theta$ ) with the step-interval of 0.02°.

The registration of <sup>1</sup>H, <sup>19</sup>F NMR spectra was performed on a Bruker Avance AV-300 solid-state NMR spectrometer within the magnetic field range of 7.04 T. A one-pulse sequence was used. In experiments with the sample rotation at the magic angle (MAR) we employed synchronized spin echo with the sample rotation frequency amounting to 15 kHz. As the reference chemical shift we used hexafluorobenzene for <sup>19</sup>F and hexamethyldisiloxane for <sup>1</sup>H, the measurement error amounted to 3 ppm, in the experiments with MAR this value was equal to 1 ppm.

The calculation of chemical shifts in <sup>1</sup>H NMR spectra was carried out with the use of Gaussian-03 software [6]. The calculations were carried out within the framework of HF method (basis 6-31G) and DFT theory (B3LYP, basis 6-311+G (d)) [7]. In order to check the optimality of choosing the calculation procedure, we performed the calculation of geometrical parameters and NMR spectra of some model fluorocarbon molecules and hexamethyldisiloxane those were taken as a base for calculating chemical shift values.

## RESULTS AND DISCUSSION

The results of analyzing the morphology of powder particles demonstrate that the initial sample consists of aggregates with the size up to ten and more micrometers, which aggregates are formed by spherical mono-particles of micrometer size (Fig. 1). The measured size distribution function (Fig. 2) can serve as a confirmation for this fact. In the processed sample, the aggregates decay to give monoparticles. The destruction of aggregates could be connected with removing a binding low-molecular fraction of PTFE and other components from the product in the course of heat treatment.

The thermogravimetric investigation has revealed differences between initial and processed samples (Fig. 3). So, for the initial sample one can observe a fast mass loss at 50–80 °C, which, most likely, could be connected with the removal of water and low-molecular hydrocarbon fractions. The mass loss level within this temperature range is equal to 12%. Within the temperature range of 80–300 °C, a slow mass decrease is observed, whereas an intense

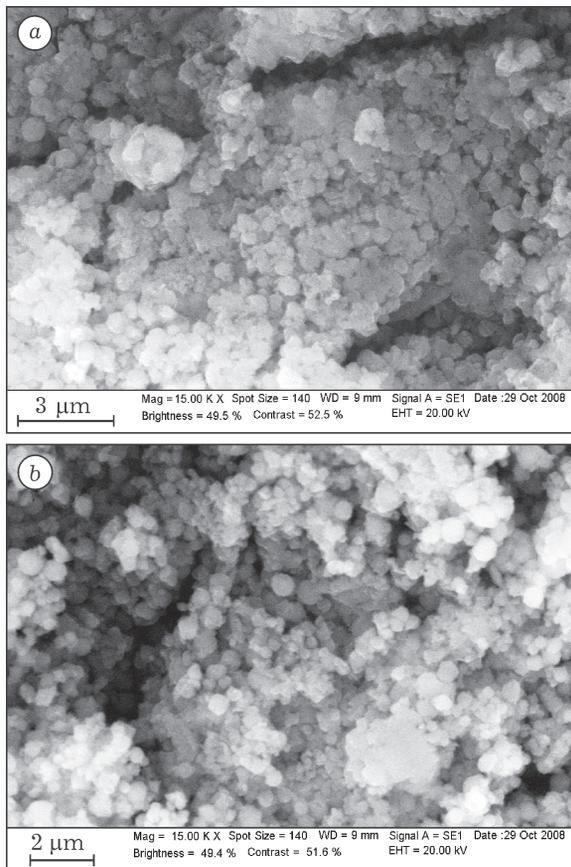


Fig. 1. SEM image for initial (a) and processed (b) samples.

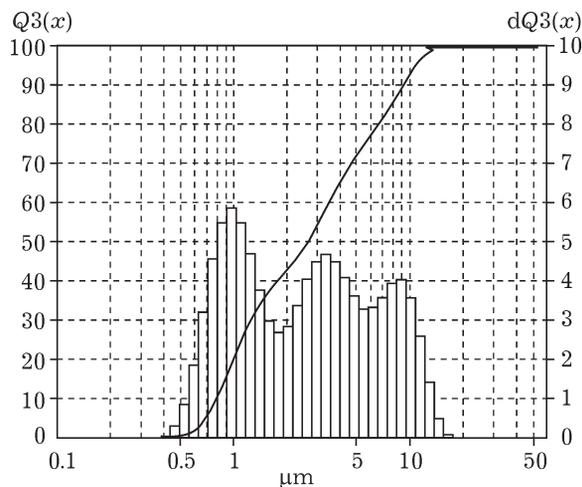


Fig. 2. Particle size distribution function and cumulative function for the initial sample powder.

mass loss is observed at the temperature values higher than 350 °C. It is not improbable that thermal destruction or evaporation of some PTFE fractions occurs within this temperature range as it is observed for the Forum trade-

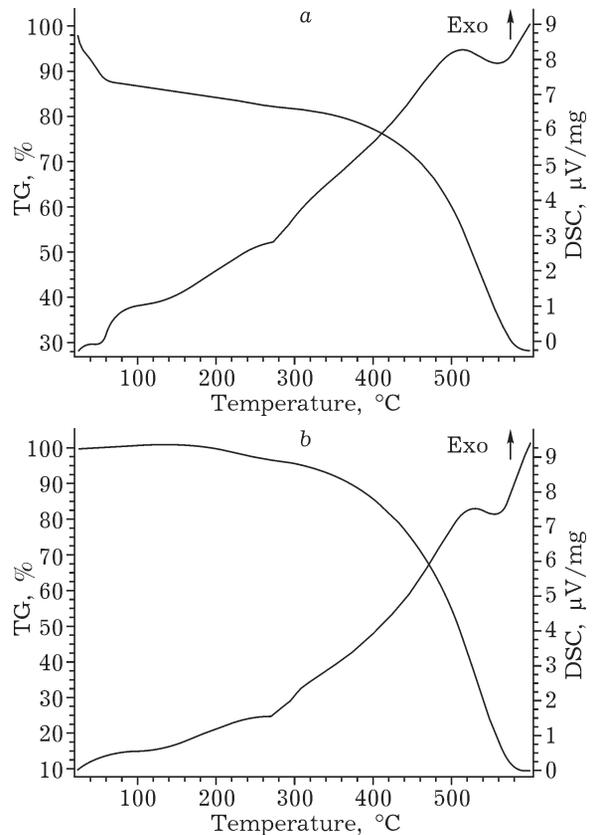


Fig. 3. Derivatographic data for initial (a) and processed (b) samples.

mark powder [8]. In the processed sample there are no changes observed on the thermogravimetric curve up to 200 °C. However, within the range of 350–575 °C one can observe an intense mass loss. For both samples the DSC curve exhibits endothermic anomalies at 280 °C, which could be connected with melting the samples. For the samples of the initial product F-4, the melting occurs at a higher temperature (>320 °C) [1]. This indicates the fact that the molecular mass of polymeric chains in the powder under investigation is lower as compared to the initial sample of F-4 powder. It is indicated also by a lower starting temperature of intense mass loss for the powders (350 °C), whereas for F-4 this process is observed at 475 °C [8].

Figure 4 demonstrates the results of X-ray diffraction studies on the processed powder. The XRD profile exhibit an intense peak inherent in PTFE at  $d/n = 4.90 \text{ \AA}$  ( $2\theta = 18.01^\circ$ ), a number of peaks of lower intensity and an amorphous halo centered at  $2\theta = 38^\circ$  [9]. The crystal phase (the symmetry group  $p6mm$ ) is formed

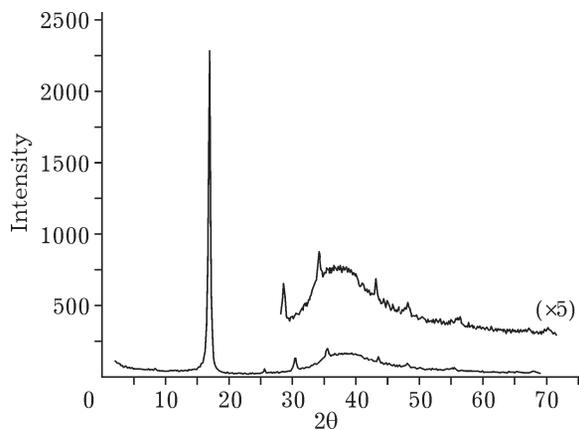


Fig. 4. X-ray diffraction profile for the processed registered at a room temperature.

by the density packing of spiral polymeric macromolecules along hexagonal axis. The XRD profiles of the sample under investigation, as opposed to the XRD profile of the initial F-4 sample, exhibit crystal peaks with nonzero value of third Miller index to disappear, which could be connected with disordering with respect to the hexagonal axis of the crystal phase [9]. The disordering is manifested in chaotic disorientation of  $\text{CF}_2$  groups forming a macromolecular chain, around hexagonal axis and in shifting the macromolecules with respect to each other. At the same time, the XRD profile of the powder under investigation coincides completely with XRD profile of the powder "Forum" except the fact that the fraction of the disordered phase characterized by halo, for the sample under investigation is greater in intensity to a considerable extent. The great disordering level for macromolecules in the sample under investigation is quite appropriate, since the technology of condensed powder obtaining is more rigid.

The features of the powder molecular structure were studied using the methods of IR spectroscopy and  $^{19}\text{F}$ ,  $^1\text{H}$  NMR spectrometry. The IR spectra of powders were similar to PTFE IR spectrum [10] and were characterized by a set of intense bands ( $505$ ,  $555$ ,  $625$ ,  $640$ ,  $1154$ ,  $1212\text{ cm}^{-1}$ ) corresponding to fluoropolymeric macromolecules (Fig. 5, *a*). Besides those, for the initial sample one can observe absorption bands centred at  $1786$  and  $1715\text{ cm}^{-1}$  inherent in terminal groups such as  $-\text{CF}=\text{CF}_2$  and  $-\text{HC}=\text{O}$  usually present in low-molecular fractions [10]. Additional bands are of low intensity (see Fig. 5, *b*), they are displayed in a much

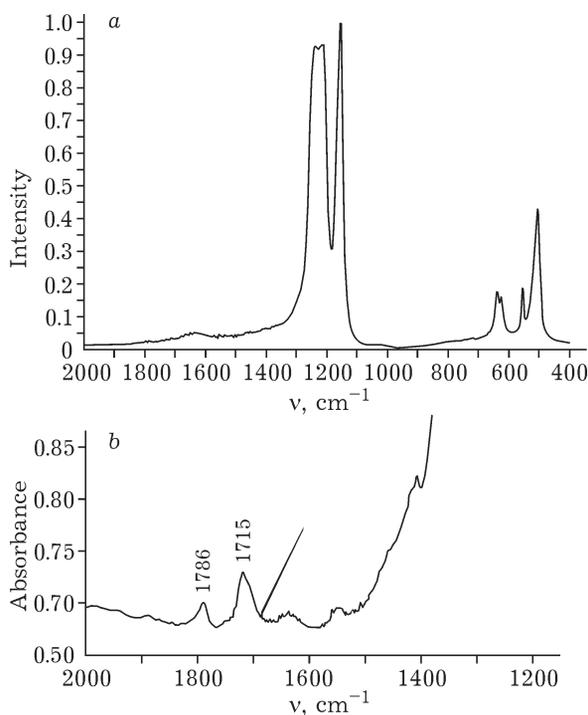


Fig. 5. IR spectra for the processed sample (*a*) and a fragment of the spectrum for the sample obtained at a higher concentration of fluoropolymer in the tablet under investigation (*b*).

weaker manner than it is in the spectra of powder "Forum", becoming visible only under special experimental conditions. This fact indicates a lower part of low-molecular fraction. The bands observed at greater wave vector values are connected with water present in KBr.

The difference of  $^{19}\text{F}$  NMR spectra for the initial sample from F-4 powder spectra consists in the presence of a line 40 ppm shifted with respect to the reference signal. This line corresponds to terminal olefin and trifluoromethyl groups [11] inherent in low-molecular fractions. The intensity of this component is much lower as compared to the spectra of "Forum" samples, which is in a good agreement with the data of IR spectroscopy. The line asymmetry observed at the right shoulder of the spectral line could be connected with chemical shift anisotropy for fluorine nuclei in  $\text{CF}_2$  groups. The spectrum half-width at a room temperature is equal to 18 kHz for the processed sample, which is a somewhat higher as compared to that for F-4 sample (16 kHz). On heating one can observe narrowing spectra for both samples: at the temperature of  $150\text{ }^\circ\text{C}$  the value of spectral width amounts to 13 and 8 kHz, respectively.

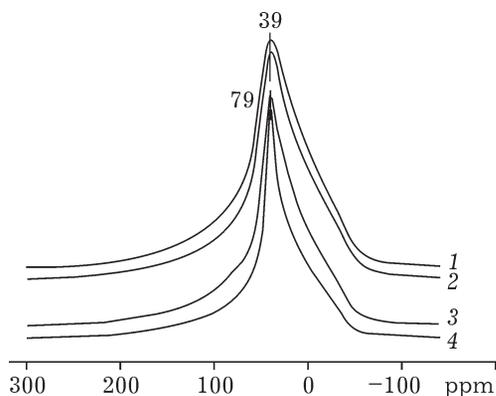


Fig. 6.  $^{19}\text{F}$  NMR spectra for the sample under investigation (1, 3) and F-4M (2, 4).  $T$ ,  $^{\circ}\text{C}$ : 27 (1, 2), 147 (3, 4).

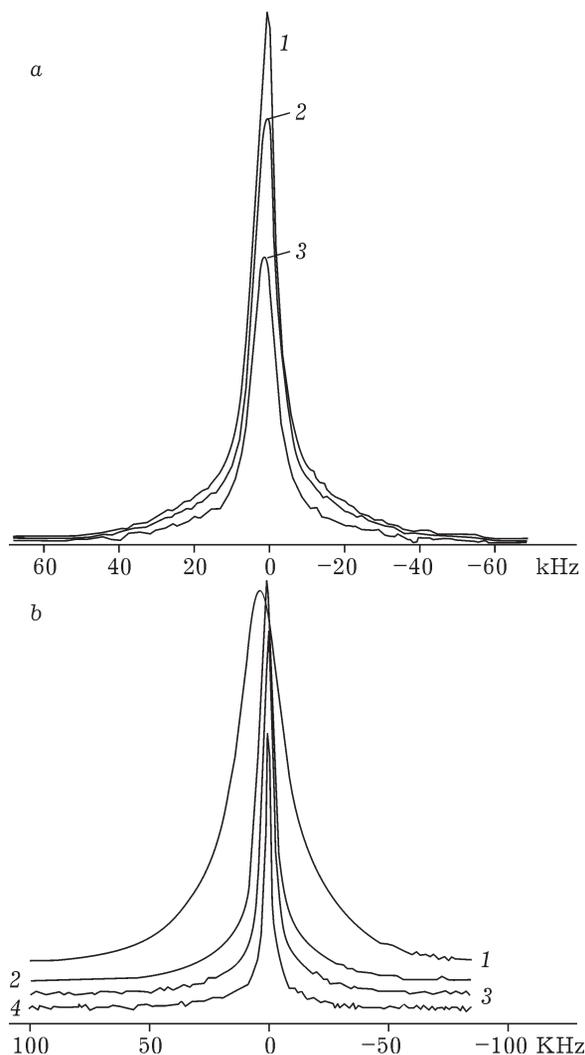


Fig. 7.  $^1\text{H}$  NMR spectra of samples (a) registered at the temperature of  $30^{\circ}\text{C}$ : 1 – initial, 2, 3 – after heating up to 150 and  $370^{\circ}\text{C}$ , respectively;  $^1\text{H}$  NMR spectra line shape (b) depending on the temperature,  $^{\circ}\text{C}$ : 110 (1), 30 (2), 150 (3), and  $370^{\circ}\text{C}$  (4).

As opposed to other PTFE powders including “Forum”, for the sample under investigation we have revealed NMR signals from protons with low intensity, which indicates the presence of molecular formations containing protons in the sample (Fig. 6). Heating the processed samples at the temperature values amounting to 150 and  $370^{\circ}\text{C}$  and the subsequent registration of spectra at a room temperature have revealed decreasing the signal intensity, which indicates partial removing the molecular formations from the samples (Fig. 7).

The low-temperature spectra of the processed sample do not exhibit any doublet structure inherent in water molecules up to the temperature of  $125^{\circ}\text{C}$ , which could indicate water absence. Indirectly this assumption is confirmed by the data concerning the second moment of low-temperature spectrum equal to  $740\text{ kHz}^2$  ( $40\text{ Gs}^2$ ), whereas the values amounting to  $\sim 1000\text{ kHz}^2$  ( $55\text{ Gs}^2$ ) are inherent in the crystallization water. The value of the second moment to a greater extent corresponds to the data inherent in methyl groups ( $430\text{--}600\text{ kHz}^2$ ) [12].

With heating a sample, the spectrum becomes more narrow, which is reflected in the temperature dependence of the second moment and spectral line width (Fig. 8) being connected with an increase both in the orientation mobility of proton-containing molecules at the temperature higher than  $70^{\circ}\text{C}$ , and in the diffusion mobility at the temperature higher than  $180^{\circ}\text{C}$ . From the temperature dependence, with the use of the Uo-Fedin equation connecting the spectral narrowing temperature ( $T_c$ ) with the activation energy  $E_a$  ( $E_a = 154.7T_c$ ), one could estimate an order of magnitude for the activation energy of molecular movement [13]. For

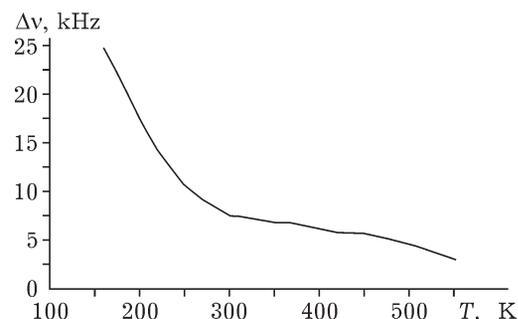


Fig. 8. Linewidth temperature dependence for  $^1\text{H}$  NMR spectrum.

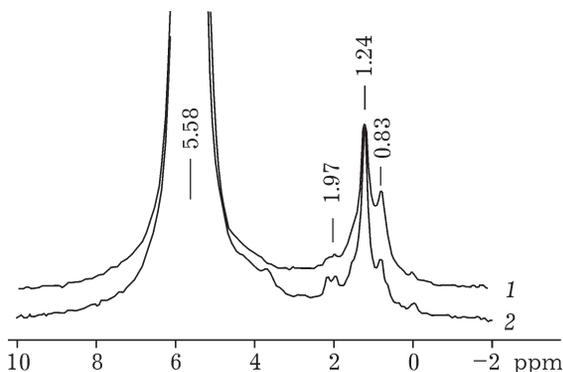


Fig. 9.  $^1\text{H}$  NMR MAR spectra for the samples registered at a room temperature: 1 – initial, 2 – after heating to 370 °C.

the orientation movement this value does not exceed 23 kJ/mol, whereas for the diffusion movement the activation energy is equal to 71 kJ/mol.

In order to elucidate the nature of molecules containing protons, we have registered  $^1\text{H}$  NMR spectra with the sample rotation at the magic angle (Fig. 9). This procedure has allowed us to increase the resolution as well as to perform numerical measurements for the chemical shifts of separate components. (Rotational satellites are not presented in Fig. 9.) The spectrum resolved represents an intense singlet with the chemical shift value of 5.58 ppm and a low-intensity multiplet consisting of overlapped lines at lower chemical shift values (1.97, 1.24, 0.83 ppm) (see Fig. 9).

The signal ascription to certain molecular groups could be performed with the help of quantum chemical calculation for resonant line chemical shifts [14]. According to theoretical estimations, the chemical shift of protons for fragment  $\text{CF}_3\text{-CF}_2\text{-CHF-CF}_2\text{-CF}_3$  coincides well with the signal value for the basic component of the spectrum (5.50 ppm). Basing on this fact one could assume, that the main form of hydrogen inclusion within the sample consists in substituting one fluorine in  $\text{CF}_2$  group by a proton. Calculations have been performed concerning chemical shifts of hydrogen-containing molecules those could be present in the sample. The signal shift value for  $-\text{C}(=\text{O})\text{CH}_3$  molecular fragment amounts to 2.01 ppm, therefore this fragment could be thoroughly attributed to one of the components of a multiplet. For the fragment  $-\text{CF}_2\text{-CF}_2\text{-C}(\text{CH}_3)_2\text{-C}(\text{CH}_3)_3$  the shift value for the methyl groups nearest to the

fluorocarbon part of a macromolecule, is equal to 1.17 ppm, whereas for remote groups this value amounts to 0.89 ppm. The data obtained also allow one to attribute them to the fragment indicated. The multiplet fraction in the general spectrum amounts to 15 % before heating and 9 % after heating, which indicates the loss of corresponding hydrogen-containing molecules in the course of heating.

It has been demonstrated earlier that the low-molecular fraction of the powder “Forum” can be dissolved in supercritical carbon dioxide ( $\text{SC-CO}_2$ ) at certain thermodynamic regimes [5]. This fact allows obtaining fluoropolymeric coatings with nanosized thickness those are capable to provide the surface superhydrophobicity. An experiment has been conducted with a number of ultrafine PTFE powders under identical technological conditions (the temperature being equal to 75 °C, pressure of 500 atm, the volume capacity of a reaction cell equal to 12 mL and the initial weighed sample portion amounting to 0.7 g). The solubility of the powder under investigation amounted to ~ 5 mass %, whereas for the powders of “Forum” and “Fluralit” trademarks this value is equal to 12 and 7 %, respectively. A lower value of solubility could be connected with a smaller amount of low-molecular components in the sample as compared to the “Forum” and “Fluralit” powders.

## CONCLUSION

The steam-hydrothermal technology for the pyrolysis of industrial wastes developed by the authors allows obtaining a commercial PTFE ultrafine powder from waste products. Experimental studies performed with the use of some physical methods and quantum-chemical calculations have revealed the features of molecular, supramolecular, crystal structure and morphology of powders. As the composition of the powder is concerned, molecular formations containing hydrogen have been revealed and identified therein. It has been established that in the powder there are both low- and high-molecular PTFE fractions present, whereas a lower molecular mass is inherent in the high-molecular fraction as compared to this value inherent in the initial PTFE whereof the pow-

der is obtained. Additional groups have been revealed in the low-molecular fraction those are rate-determining with respect to the growth of macromolecules, with providing the polymer branching. The presence of the crystal and disordered phases has been revealed; the former exhibits structural features connected with rotational disordering of  $\text{CF}_2$  groups along the hexagonal axis. The fraction of the disordered phase in the powder under investigation is much higher than it is in the Forum trademark powder obtained via the thermal gas-dynamic method. The shape of powder particles is close to spherical, and one could observe the formation of agglomerates consisting of separate particles. Basing on the obtained data concerning the structure of the powder we may believe that after the thermal processing the powder could be used as a resource-saving additive for lubricating oils, as well as in order to obtain composites based on fluoropolymers.

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