doi:10.20944/preprints202109.0350.v1

Structure of Polytetrafluoroethylene Modified by the Combined Action of γ-Radiation and High Temperatures

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Keywords: PolyTetraFluoroEthylene, Ionizing radiation, High temperatures, Modification, Crystallization, Cross-linking, Pore, Structure

By means of X-ray computed microtomography (XCMT) the existence of a developed microporous structure having an average pore diameter of ~3.5 μm and pore content of ~1.1 vol.% has been revealed in unirradiated polytetrafluoroethylene (PTFE). It has been found that the combined action of gamma radiation (absorbed dose per PTFE of ~170 kGy) and high temperatures (327-350 °C) leads to the disappearance of the microporous structure and the formation of several large pores with sizes from 30 to 50 μm in the bulk of thermal-radiation modified PTFE (TRM-PTFE). It has been established by X-ray diffraction (XRD) analysis that the thermal-radiation modification of PTFE leads to an increase in the interplanar spacings, the degree of crystallinity and volume of the unit cell, as well as to a decrease in the size of crystals and the X-ray density of the crystalline phase in comparison with the initial polymer. It is assumed that the previously established effect of improving the deformation-strength and tribological properties of the TRM-PTFE can be due not only to the radiation cross-linking of polymer chains but also to the disappearance of the micropore system and to the ordering of the crystalline phase of PTFE.

1. Introduction

High-temperature radiation modification of polytetrafluoroethylene (PTFE) is a promising method for overcoming the disadvantages of this material – such as cold brittleness, porosity, and low radiation resistance [1, 2]. It was found [3-6] that the combined action of various types of ionizing radiation (γ-radiation, electrons of different energies) and temperatures exceeding the melting point of polymer crystallites can improve the tribological and deformation-strength characteristics of PTFE, change its spectral-luminescent properties, and increase the radiation resistance.

A common drawback of cited studies [1–6] is the lack of estimates of the parameters characterizing the newly formed three-dimensional network - such as the density of the cross-links and the molecular weight of the TRM-PTFE between cross-links [7]. The conclusion about the occurrence of radiation-induced cross-linking processes during irradiation of PTFE melt is made mainly on the basis of measurements of the deformation-strength and/or tribological characteristics of the thermal–radiation modified polymer [1–6].

The lack of estimates of the density of cross-links, - which is a key parameter characterizing the efficiency of radiation cross-linking processes, excludes the comparison of experimental data with the predicted efficiency of the high-temperature irradiation treatment of PTFE [1–6]. This may be due to the high chemical inertness of PTFE, which makes it difficult to estimate the density of cross-links in TRM-PTFE using the Charlesby–Pinner equation [7].

At the same time, it is known that traces of the crystalline phase of PTFE can exist in the melt up to a temperature of 400 °C and that the processes of radiative gas evolution and depolymerization under γ-irradiation of PTFE up to 500 °C proceed [8, 9]. Therefore, it can be assumed that the irradiation of PTFE in the melt is accompanied by the occurrence of competing processes of radiation destruction and cross-linking, crystallization, gas evolution, etc.

It has been shown that under the conditions of simultaneous cross-linking and crystallization processes, the cross-link density can be estimated from the average crystallite size [10]. Then, it is relevant to carry out the X-ray diffraction study of radiation-induced changes in the crystalline phase of the initial and TRM-PTFE [11].

The aim of this study is to establish the nature of the effects of improving the deformation-strength and tribological properties, increasing the radiation resistance of PTFE under the combined action of ionizing radiation and high temperatures by studying the microstructure and crystalline phase of the initial and thermal–radiation modified polymer.

2. Material and methods

2.1. Materials

For the manufacture of TRM-PTFE and control samples, PTFE grade F-4 (Soviet State Standard 10007-80) produced by JSC “HaloPolymer Kirovo-Chepetsk”

(Kirovo-Chepetsk, Perm’ Region, Russian Federation) was used in the form of cylindrical rods 25 mm in diameter and 250 mm in height, which were obtained by sintering powdered PTFE obtained by emulsion polymerization.

Disks with a diameter of 25 mm and a thickness of 2 mm, which were cut from cylindrical rods of the initial and TRM-PTFE, were used for X-ray diffraction studies. The X-ray computed microtomography study of the microstructure of initial and TRM-PTFE was carried out on cylindrical polymer samples with a diameter of 3 mm and a height of 6 mm.

2.2. Radiation modification and dosimetry

The thermal–radiation modification of PTFE blanks by exposure to γ-radiation of the ^{60}Co isotope (mean energy 1.25 MeV) was implemented in a radiation-chemical apparatus made of stainless steel and located in the working chamber of the unique scientific installation (USI) "Gammatok" at the Institute of Problems of Chemical Physics, Russian Academy of Science [12]. Irradiation was performed in the nitrogen environment at a temperature from 327 to 350 °C and a dose rate of 3 Gy/s to an absorbed dose of 200 kGy. After radiation treatment, the TRM-PTFE sample was cooled to room temperature in the working chamber of the USI "Gammatok". Control samples of initial PTFE were irradiated under similar conditions, but at a temperature of 60°C.

The dose rate and absorbed dose were determined using the Fricke method in accordance with the requirements of Russian State Standard 34155-2017. To take into account the difference between the electron densities of the Fricke dosimetric solution and PTFE, when calculating the dose absorbed by the polymer, a correction factor (0.865) was introduced according to Soviet State Standard 27602-88. Therefore, the dose absorbed by PTFE under the described irradiation conditions was 200 × 0.865 = 173 kGy. Since the dose rate is determined by the

Fricke method with an accuracy of 20%, and the PTFE preform during the irradiation was surrounded by a stainless steel layer, it can be assumed that the condition of electronic equilibrium during the thermal–radiation modification of PTFE is fulfilled.

2.3. X-ray computed microtomography measurements

X-ray computed microtomography investigations of the three-dimensional structure in initial polymer and TRM-PTFE in the submicron range (resolution limit 0.7 μm) were carried out using an FEI HELISCAN MICRO-CT X-ray microtomograph.

2.4. X-ray diffraction pattern measurements

The X-ray diffraction study of PTFE and TRM-PTFE crystal structure was carried out at room temperature using a DRON-3M diffractometer (Cu K_α radiation with a characteristic wavelength of λ_{Cu} = 1.5406 Å, the scanning interval of diffraction angles 2θ from 5 to 80°, the scanning step from 0.05 to 0.02°, exposure from 1 to 20 s). The degree of crystallinity of the studied PTFE samples was determined from the X-ray diffraction data, as well as by differential scanning calorimetry measurements according to [11].

2.5. Density measurements

The density of the initial polymer and TRM-PTFE was determined by hydrostatic weighing with an accuracy of 0.001 g/cm^3. The change in the mass of the sample before and after the test was determined by weighing on an AND microbalance (model GR 202, Japan) with a readability of 0.01 mg.

3. Results

3.1. Observation of the porous structure and its disappearance after thermal-radiation modification in Polytetrafluoroethylene

It was found from the X-ray computed microtomography measurements that the initial PTFE contains numerous micropores, which, probably, could arise during sintering of the polymer sample (Figs. 1a, 2a) [13]. The sizes of micropores varied from 1 to 12 μm and the size distribution maximum was at 3.5 μm. By integrating the pore size distribution function, the porosity of the initial PTFE sample was estimated to be ~1.1% (Fig. 1b).

The subsequent thermal–radiation modification of PTFE leads to an almost complete disappearance of micropores (Fig. 2b). Several large pores with sizes from 20 to 50 μm can be observed in the sample volume, which indicates the dissolution and/or coalescence of micropores in the process of thermal–radiation modification of PTFE. In this case, the gases contained inside the micropores are released from the polymer melt into the environment [9].

3.2. Characterization of X-ray diffraction patterns registered for initial and thermal-radiation modified Polytetrafluoroethylene

High-temperature radiation modification has no significant effect on the properties of PTFE X-ray spectrum. Diffraction patterns of the initial polymer and TRM-PTFE in the range of diffraction angles 2θ from 5 to 80° contained 13 and 12 Bragg peaks, respectively, as well as three haloes in the ranges 2θ = 10°–25° (I), 25°–70° (II) and 72°–75° (III) (Table 1, Figs. 3, 4a, 4b).

The diffraction patterns of the initial and TRM-PTFE were indexed by the method described in [14–16], taking into account the reference data (protocol JCPDS No. 47-2217 [17]) and the results previously obtained in [18–20]. The procedure for determining the degree of crystallinity X_c of polymers was described earlier [11]. The interplanar spacing d_{hkl} and the average crystal size L in the initial polymer and TRM-PTFE were calculated using the well-known Wulff–Bragg condition and Debye–Scherrer equation (Tables 1, 2) [14].

It is usually considered that PTFE crystals at room temperature belong to the hexagonal system with the unit cell containing 15 CF_2 groups packed into a spiral with 7 turns around the hexagonal axis [14–20]. Gamma-irradiation of PTFE up to 173 kGy with simultaneous exposure to temperatures in the range of 327–350°C leads to the shift of almost all diffraction maxima towards smaller diffraction angles (Table 1). The shift is from 0.042° (diffraction maximum *hkl* = 1015) to 0.311° (*hkl* = 220).

The diffraction maximum *hkl* = 100 dominates in the X-ray spectra of the initial polymer and TRM-PTFE (Fig. 3, Table 1). Because of thermal–radiation modification, the amplitude of the diffraction maximum hkl = 100 decreases by ~10% and its width increased (the full width at the half-maximum (FWHM) increases by ~0.366°).

It was shown that the diffraction maximum *hkl* = 100 consists of two components, which correspond to PTFE crystals belonging to the hexagonal system, but having different interplanar spacings [11]. By approximating the spectral shape of the diffraction maximum under study with two Gaussians, it was found that the maxima of the components of peak *hkl* = 100 are located at $2\theta = 18.027° \pm 0.003°$ and $18.087° \pm 0.001°$ for the initial polymer and at $17.832° \pm 0.006°$ and $18.007° \pm 0.001°$ for TRM-PTFE.

In this case, the shift toward smaller diffraction angles for the first and second components was ~0.195° and ~0.08°, respectively. Consequently, the thermal–

radiation treatment leads to an increase in the interplanar spacings d_{hkl} of both types of PTFE crystals, but this increase turns out to be different in them.

It was shown that reflection in the region $2\theta \approx 18°$ can be attributed to intermolecular scattering by PTFE macromolecules containing conformational defects [18]. Then, it can be concluded that the shift towards smaller reflection angles in the X-ray spectra of TRM-PTFE is due to a decrease in the concentration of conformational defects caused thermal–radiation modification.

This conclusion is confirmed by the data presented in Table 1: the dominance of equatorial reflections ($l = 0$) in the range of diffraction angles $2\theta = 30°–70°$ on the diffraction patterns of the initial polymer and TRM-PTFE can be attributed to disordering along the hexagonal axis of the PTFE unit cell (space group P6mm) [19]. It is known that the crystal structure of PTFE is based on the close packing of spiral polymer molecules along the hexagonal axis [18–20]. However, in the course of crystallization, the CF_2 groups that form the PTFE unit cell can be disordered with respect to the rotation angle around the hexagonal axis and the monomer units of the polymer chains that form the PTFE unit cell can be shifted with respect to each other.

Obviously, γ-irradiation of PTFE in the melt leads to a significant decrease in the concentration of conformational defects in polymer chains and to the ordering of the crystal structure. It should be note that a similar conclusion was made when studying the crystal structure of PTFE irradiated by a proton flux with energy of 4 MeV [21].

It is known that PTFE is characterized by the spherulite crystal structure in the form of expanded chain crystals with very thick lamellas (~1000 Å) [21]. Lamellar surfaces refer to ($h0l$) reflection planes, where the angle between the direction of the polymer chain and the normal direction of the lamella varies from 20° to 40°

doi:10.20944/preprints202109.0350.v1

[22]. In the considered range of diffraction angles of the X-ray spectrum of PTFE, the diffraction maxima with *hkl* = 107 and 108 satisfy the requirement for reflection from the lamella surface (Figs. 4a, 4b). The combined action of ionizing radiation and high temperatures results in a decrease in the relative intensity of the diffraction maxima 107 and 108 by ~3% (Table 1, Figs. 4a, 4b).

Within the framework of the three-phase model of an amorphous–crystalline polymer, the structure of PTFE can include crystalline, amorphous, and smectic phases [22]. In polyethylene and in poly-L-lactic acid, the smectic phase is a layer of partially ordered polymer chains around the lamella, which has a thickness of ~ 40–50 Å [22, 23]. Possibly, the smectic phase can also be formed on the walls of lamella as well as micropores in PTFE. Then, a decrease in the intensity of diffraction maxima 107 and 108 in the X-ray spectra of TRM-PTFE (Table 1, Figure 4 a, b) may be attributed to a decrease in the content of the smectic phase in the composition of PTFE due to the disappearance of micropores and the transformation of lamellae into fibrils [24].

This conclusion is confirmed by the scanning electron microscopy data [25], which indicate that irradiation at temperatures exceeding 200°C leads to the thickening of lamellae in PTFE and to the formation of a fibrillar structure. As noted above, the consolidation of lamellae will be accompanied by a decrease in the lamella surface area following by a decrease in the intensity of the diffraction maxima *hkl* = 107 and 108 in the X-ray scattering spectrum of PTFE.

In the X-ray scattering spectra of PTFE, the amorphous phase is characterized by a diffuse diffraction maximum in the region of 10°–25° [11, 18]. Gamma-radiation-induced modification of PTFE at high temperatures leads to an insignificant increase (~5%) in the integral intensity of the diffuse diffraction maximum I, and, consequently, in the content of the amorphous phase in the polymer (Table 3).

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The origin of halo II can be attributed to intramolecular scattering from disordered polymer chains with a conformation close to that of PTFE crystals, but not included in the crystalline phase; presumably, these macromolecules are included in the smectic phase of the polymer [18, 20]. The spectral shape of halo II can be approximated by two Gaussians (Table 3, Figure 4, a, b), which suggests the existence of two independent non-crystalline components in the smectic phase of PTFE, the first of which includes partially ordered PTFE macromolecules, and the second, disordered layers of specific structural formations, so-called hexagons [18]. This agrees with the conclusion made in [24], where the nature of halo II was attributed to the presence of low molecular weight impurities in the polymer. Possibly, the origin of halo II can be attributed to the presence of micropores (more accurately, to the presence of a smectic phase on the surface of micropore walls) [25].

Using the Debye–Scherrer equation, the size of scattering centers providing the appearance of the first and second components of halo II on the diffraction pattern of PTFE was estimated to be equal 10.06 and 5.65 Å for the initial polymer and 9.69 and 5.16 Å for TRM-PTFE, respectively. As a whole, it can be concluded that the combined action of γ-radiation and high temperatures provides no noticeable changes in the characteristics of the halo II components in the X-ray spectra of the initial polymer and TRM-PTFE.

The nature of halo III in the range of diffraction angles 72°–75°, observed in the X-ray spectrum of PTFE, is attributed to scattering by polymer macromolecules with a 15/7 helix conformation [20]. Unfortunately, a high “signal-to-noise” ratio characteristic of this region of the recorded X-ray spectra of PTFE does not allow certain conclusions about the effect of thermal–radiation modification on the characteristics of halo III; at least, it was assumed that they also change insignificantly (Table 3).

3.3. Determination of the lattice parameters for initial and thermal-radiation modified Polytetrafluoroethylene by means of Hull-Davey chart

In the hexagonal structure of PTFE crystals, the interplanar spacings d_{hkl} are related to the lattice constants $a = b$ and c as [14–16]:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \cdot \frac{h^2+hk+k^2}{a^2} + \frac{l^2}{c^2} \tag{1}$$

Let us transform Eq. (1) in accordance with [15, 16] to determine the parameters of the unit cell of the initial polymer and TRM-PTFE:

$$2\log(d_{hkl}) = 2\log a - \log\left[\frac{4}{3}(h^2 + hk + k^2) + \frac{l^2}{(c/a)^2}\right] \tag{2}$$

Next, we write Eq. (2) for two reflection planes of a hexagonal PTFE crystal (0015 and 1015, Table 1), and subtract one equation from the other:

$$2\log d_{0015} - 2\log d_{1015} = -\log\left[\frac{4}{3}(h_1^2 + h_1k_1 + k_1^2) + \frac{l_1^2}{(c/a)^2}\right]\cdots$$

$$\cdots + \log\left[\frac{4}{3}(h_2^2 + h_2k_2 + k_2^2) + \frac{l_2^2}{(c/a)^2}\right] = -F_1 + F_2 \tag{3}$$

Here, the difference between interplanar spacings for reflections 0015 and 1015 does not depend on the lattice constant a. The graphical solution of Eq. (3) is the so-called Hull–Davey diagram, which is a log–lin plot of the parameter $F = 4(h^2 + hk + k^2)/3 + l^2/(c/a)^2$ as a function of the ratio c/a (Fig. 5) [15, 16]. Then, the point of intersection of the straight lines corresponding to the difference $\Delta = 2\log(d_{0015}) - 2\log(d_{1015})$ for the initial polymer and TRM-PTFE with the dependence describing the difference $F_2 - F_1$ on c/a will determine the desired ratio of the lattice constants of PTFE (Fig. 5, curves 3–5, Table 2).

The lattice constant a of PTFE crystals was determined using the equation

$$\frac{a^2}{d_{hkl}^2} = \frac{4}{3} \cdot (h^2 + hk + k^2) + \frac{l^2}{(c/a)^2} \tag{4}$$

The lattice constant a can be determined from the slope of the dependence Y = $[(4/3) \times (h^2 + hk + k^2) + l^2/(c/a)^2]$ ¤ $1/d_{hkl}^2$ (Fig. 6). It was found that the thermal–radiation modification of PTFE leads to an insignificant increase in the lattice constant *a* by ~ 0.1 Å and to an insignificant decrease in the large lattice constant *c* also by ~ 0.1 Å (Table 2).

3.4. Comparative analysis of the experimentally established as well as obtained from X-ray data density values of the initial and thermal-radiation modified Polytetrafluoroethylene

The volume of the unit cell and the X-ray density of the initial polymer and TRM-PTFE were calculated using the expressions [14]

$$V = 0{,}866a^2c \tag{5}$$

$$\rho_\mathrm{c} = \frac{M}{N_A V} \tag{6}$$

- where M = 0.75 kg/mol is the molar mass of PTFE [20] and N_A is the Avogadro number. As follows from Table 2, the volume of the unit cell in TRM-PTFE increases, which can be due to an increase in interplanar spacings in the crystalline phase of PTFE after gamma-radiation modification at high temperatures (Table 1). An increase in the volume of the unit cell in TRM-PTFE is accompanied by a decrease in ρ_c, despite an increase in the degree of crystallinity of PTFE (Table 2).

Along with an insignificant increase in the degree of crystallinity in TRM-PTFE, a decrease in the average crystallite size *L* by a factor of 3.82 relative to initial PTFE is observed (Table 2). A decrease in *L* can be attributed to both the destruction of PTFE crystals during irradiation [28] as well as to crosslinking processes, which can restrict the polymer crystal growth during cooling of the melt [29].

The value of ρ_c for PTFE given in Table 2 is in good agreement with the previously obtained values 2.302 g/cm^3 [30] and 2.300 g/cm^3 [31]. It should be emphasized that the combined action of high temperatures and γ-radiation leads to a decrease in the density of the modified polymer relative to PTFE.

Apparently, the value ρ_c=2.69 g/cm^3 for PTFE, calculated in [20], is overestimated. This may be due to the error in determining $2\theta_{max}$=16.28° for the diffraction maximum *hkl* = 003 used to calculate the large lattice constant of PTFE *c* = 16.8 Å, which further led to the underestimated volume of the PTFE unit cell (~ 470 Å^3), in comparison with the data given in Table 2, and, further, to the overestimated degrees of crystallinity of the polymer.

However, the large lattice constant established in [20] is in good agreement with the value of this constant for PTFE macromolecules with the triclinic conformation (a = 5.59 Å, c = 16.88 Å, γ = 119.3°) [32]. Then, it can be assumed that the crystalline phase of PTFE contains crystals in both the hexagonal and triclinic conformations.

It should be noted that the presence of crystals in the triclinic conformation in the crystalline phase of PTFE, which determine its composition in the temperature range below a phase transition temperature of 19°C, can significantly increase the density of PTFE [32]. At the same time, when studying the structure of composite materials based on TRM-PTFE filled with silicon dioxide particles, it was shown that the phase transitions in PTFE are “smoothed” [33]. Consequently, the crystalline phase in PTFE at room temperature can consist of both "triclinic" and "hexagonal" crystals, which possibly form observed two components of the diffraction maximum *hkl* = 100 in the X-ray spectra of PTFE. Therefore, it can be assumed that the previously obtained estimates of the large lattice constant c and the X-ray density of PTFE confirm this fact [20].

Thus, the thermal–radiation treatment of PTFE can lead to a decrease in the content of triclinic crystals and an increase in the content of hexagonal crystals in the crystalline phase of the polymer. Then, the X-ray density of TRM-PTFE should be lower than ρ_c of PTFE, which was confirmed experimentally (Table 2).

Using the known estimates of the density ρ_a of the amorphous phase in PTFE (2.056 and 2.040 g/cm$_3$ in [30, 31], respectively), the density ρ of the initial polymer and TRM-PTFE can be calculated using the relationship

$$\rho_i = \rho_{ci}X_{ci} + \rho_{ai}(1 - X_{ci}) \tag{7}$$

where i = 1, 2 for the initial polymer and TRM-PTFE, respectively. The calculations were performed with $\rho_{a1}=\rho_{a2}=2.05$ g/cm^3. As follows from Table 2, the calculated values of the polymer density are in satisfactory agreement with the experimentally obtained data on the density of the initial polymer and TRM-PTFE. The somewhat higher value of the theoretical estimate of the PTFE density in comparison with the experimentally obtained one may be due to the presence of the closed micropores in the bulk of the sample.

4. Discussion

In conclusion, let us discuss the nature of the effect of improving the deformation-strength and tribological properties, as well as increasing the radiation resistance of PTFE, caused by thermal radiation treatment [1–6]. It is easy to estimate the density of cross-links in the polymer from the average size of the TRM-PTFE crystals ~1.32×10^{18} cm^{-3} (Table 2) [10]. However, in the case of acetylene-sensitized radiation crosslinking of PTFE, it was shown that noticeable changes in PTFE physical and mechanical properties begin at a crosslink density of ~10^{21} cm^{-3} [34]. Therefore, the assumption [1–6] about the radiation crosslinking of polymer chains during high-temperature radiolysis of PTFE, as the main reason for improving the operational properties of the material, is doubtful.

As follows from the results of this work, the combined action of γ-radiation and high temperatures leads to the disappearance of micropores and the ordering of the crystalline phase of PTFE due to the removal of defective crystals, which may have the triclinic conformation. In this case, the degree of crystallinity increases and the size of PTFE crystals decreases, which can be significant for improving the deformation-strength and tribological characteristics of the polymer.

The conclusion about the high radiation resistance of TRM-PTFE [1–6] is erroneous, since the radiolysis of the unmodified polymer proceeds in a heterogeneous mode [35], due to the presence of the micropore system found in this study. The dissolution and coalescence of micropores in the course of thermal–radiation modification of PTFE leads to the implementation of a homogeneous regime of radiolysis of TRM-PTFE during repeated irradiation, and an increase in the radiation resistance of the polymer in terms of mechanical properties. Obviously, the comparison of the radiation resistance of PTFE, performed disregarding the mode, in which the polymer radiolysis proceeds, is incorrect [1–6].

In addition, the dependence of the strength characteristics of solids on the porosity is known [36]. Therefore, the removal of micropores from the bulk of the polymer makes it possible to immediately improve the deformation and strength characteristics of TRM-PTFE.

5. Conclusion

The study of changes in the microstructure and structure of the crystalline phase of PTFE caused by the combined action of γ-radiation and high temperatures have provided the following conclusions:

i) The existence of a developed microporous structure with an average pore diameter of ~3.5 µm and a pore volume content of ~1.1% in PTFE has been revealed by the technique of X-ray computed microtomography. The thermal–radiation modification of PTFE leads to the disappearance of the microporous structure and the formation of several large pores with sizes from 30 to 50 µm.

ii) A comparative study of the diffraction patterns of the initial polymer and TRM-PTFE has been carried out by the method of X-ray diffraction analysis. It has been established that the combined action of γ-radiation up to a dose of 173 kGy and high temperatures leads to an increase in interplanar spacings, the degree of crystallinity, and volume of the unit cell and to a decrease in the size of crystals and the X-ray density of the crystalline phase in TRM-PTFE in comparison with the unmodified polymer. All found differences have been explained under the assumption that the phase transition in the crystalline phase of PTFE at 19°C is smoothed; as a result, crystals of triclinic and hexagonal conformations can be present in PTFE at room temperature.

iii) Thermal–radiation modification leads to the removal of crystals in the triclinic conformation, to an increase in the contribution of hexagonal crystals, and to local ordering of the TRM-PTFE structure. Satisfactory agreement between the calculated and experimentally determined values of the density of the initial polymer and TRM-PTFE confirms the assumption about the presence of two types of lattices in the crystalline phase of PTFE

iv) The effect of improving the deformation-strength and tribological properties of PTFE caused by the combined action of ionizing radiation and high temperatures is due not only to the processes of radiation cross-linking of polymer chains but also to the disappearance of the micropore system and the ordering of the crystalline phase of PTFE. Radiation crosslinking processes can affect the growth and size of the resulting PTFE crystals.

v) Averaging of the properties of PTFE under the combined action of the high temperatures and gamma-irradiation is the main reason for a significant increase in the radiation resistance of the thermal–radiation-modified polymer.

CRediT authorship contribution statement

Alexander S. Smolyanskii: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Visualization. **Ekaterina D. Politova:** Methodology, Validation, Formal analysis, Investigation, Writing – original draft. **Ol'ga A. Koshkina:** Conceptualization, Supervision, Validation, Writing – review & editing. **Mikhail A. Arsentyev:** Methodology, Formal analysis, Writing – review & editing. **Pavel P. Kusch:** Methodology, Formal analysis, Writing – review & editing. **Lev V. Moskvitin:** Methodology, Formal analysis, Writing – review & editing. **Sergeii V. Slesarenko:** Resources, Writing – review & editing. **Dmitrii P. Kiryukhin:** Resources, Supervision, Validation, Methodology, Formal analysis, Writing – review & editing. **Leonid I. Trakhtenberg:** Conceptualization, Resources, Supervision, Validation, Project administration, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study was carried out by order of the Ministry of Higher Education and Science of the Russian Federation (State assignment No. 45.22, registration number AAAA-A18-118012390045-2) using the unique scientific installation "Gammatok-100" of the Institute of Applied Chemical Physics of the Russian Academy of Sciences within the framework of performing the State assignment AAAA-A19-119041090087-4.

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