

A New Antifriction and Sealing Material Based on Radiation-Modified Polytetrafluoroethylene

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Received February 1, 2008

Abstract—The current situation with research into the effect of ionizing radiation exposure on the structure and properties of polytetrafluoroethylene was analyzed. New methods of radiation-induced modification, that improve the performance characteristics of polytetrafluoroethylene, were discussed. The results of research into properties of polytetrafluoroethylene irradiated at temperatures exceeding the melting point of its crystalline phase in media with different compositions were presented. It is shown that, under certain irradiation conditions, an extremely strong increase (up to 10 000-fold) in the wear resistance of polytetrafluoroethylene can be achieved, with the creepage decreased up to 100-fold. A conclusion was made that high-temperature radiation-induced modification can yield new modifications of the polymer, in which the advantages offered by untreated polytetrafluoroethylene are combined with high mechanical and triboengineering characteristics.

DOI: 10.1134/S1070363209030438

Polytetrafluoroethylene (technical name fluoroplastic-4, F-4) is superior in the set of physicochemical and mechanical properties to all the known polymers. At the same time, it suffers from essential drawbacks that prevent it from more extensive application. First, it is characterized by high creep (cold flow). Irreversible plastic strain is developed in polytetrafluoroethylene at small loads, much lower than tensile strength, and at low temperatures, under glass transition point. For example, at room temperature and a load of 10 MPa (which is 2–3 times lower than the tensile strength of polytetrafluoroethylene), irreversible strain (over 200%) is developed within 100 h [1]. Second, polytetrafluoroethylene has a low wear resistance: Despite a very small friction coefficient, the wear intensity proves to be inadmissibly high [2]. Both these drawbacks are responsible for the need in frequent repair of friction units and seals made of polytetrafluoroethylene. The third drawback suffered by polytetrafluoroethylene is an extremely low radiation resistance. The limiting radiation dose in exploitation is 10 kGy, which is 2–3 orders of magnitude lower than that typical for other polymers. All this makes polytetrafluoroethylene virtually unsuitable for special technical, as well as space and nuclear power engineering applications.

The world experience suggests that these drawbacks can be eliminated by two major methods, physical modification and chemical modification. The former method implies preparation of composite materials by introduction into polytetrafluoroethylene of finely dispersed (since recently, ultradispersed and nanosized) fillers (graphite, coke, cut fiberglass and carbon fiber, metal oxides, nanodiamonds, etc.) [2]. The latter method consists in copolymerization of tetrafluoroethylene with a different, partly or completely fluorinated, monomer [3, 4]. Both these methods allowed preparation of a series of new materials with an improved, relative to initial polytetrafluoroethylene, characteristic, but ranking below polytetrafluoroethylene in a number of other properties.

These composite materials are distinguished by higher wear resistances and better elastic properties, but lose advantages in terms of antifriction and dielectric properties, as well as in adhesion, chemical and biological resistances.

Fluorine-containing copolymers are mostly used as structural materials. Importantly, by contrast to polytetrafluoroethylene, they can be processed by extrusion and pressure molding, which allows manufacture of items with intricate geometries. At the

same time, fluorine-containing copolymers have low wear resistances and are unsuitable as antifriction materials. The copolymers (F-4MB, F-40, F-42) exhibit improved physicomechanical characteristics, but rank below polytetrafluoroethylene in thermal stability, as well as in antifriction and dielectric properties.

Radiation-Chemical Modification of Polytetrafluoroethylene

Until very recently, there has existed an opinion that everything possible has already been achieved and no significant progress can be expected in the field of materials science as regards polytetrafluoroethylene and composites thereof. For example, $1.0 \pm 0.2 \text{ mg h}^{-1}$ is clearly the limiting wear resistance for composites, which parameter has not been improved as yet by varying the composition or type of the filler, in particular, nanoparticles. The same is true of tetrafluoroethylene copolymers.

However, the recent 10–15 years have brought results, unexpected in terms of conventional views of radiolysis of polytetrafluoroethylene, which open new prospects of its modification.

Radiation-chemical approaches were already applied in attempts to increase the wear resistance of polytetrafluoroethylene. For example, Istomin and Semenov [5] showed that γ -radiation exposure of the polymer at room temperature in air at atmospheric pressure causes a significant (approximately 20-fold at the absorbed dose of 500–600 kGy) decrease in the mass wear of the material. However, the atmospheric molecular oxygen sensitizes radiation-oxidation chain degradation of polytetrafluoroethylene, thereby producing a sharp decrease in strength until the samples fail at a dose of 1000 kGy.

Also, a method was proposed for preparation of wearproof polytetrafluoroethylene by γ -radiation exposure in the absence of oxygen in an acetylene medium at 20–100°C, pressure of 0.01–0.15 MPa, and absorbed dose of 30–60 kGy [6]. As a result, the wear resistance increased by three orders of magnitude relative to the initial polymer. A shortcoming of this method consists in the need to incorporate hydrocarbon modifier (acetylene) into the polytetrafluoroethylene bulk, which decreases the chemical and thermal stabilities of the polymer and is nonuniformly spread in the bulk. Moreover, this substantially deteriorates the physicomechanical characteristics,

since, whatever the composition of the medium, the radiation exposure under the mentioned conditions is accompanied by the polymer chain scission reaction with a fairly high yield, which is practically unacceptable. Also, this causes insufficiently high (by three orders of magnitude only) increase in wear resistance.

Polytetrafluoroethylene was subjected to radiation-induced modification in order to improve its performance characteristics as sealing material. Using the procedure of radiation treatment in an oxygen-free medium [7], sealing items made of polytetrafluoroethylene were irradiated at 50–55°C in an inert atmosphere up to the absorbed dose of 8 kGy. This allows increasing several times the service life of the sealing items without significantly affecting their physicomechanical characteristics.

The above-mentioned studies, as well as other research efforts dedicated to interaction of polytetrafluoroethylene with ionizing radiations [8, 9], showed that, in the context discussed, the radiation-based method is not promising.

It should be noted that the first research efforts dedicated to the action of radiation exposure on polytetrafluoroethylene date back to the 1950s [10–12]. Yanova and Taubman [12] revealed a specific behavior of this polymer upon radiation exposure at temperatures above the melting point. Abramova et al. [13] reported that, contrary to expectations, no deterioration of the physicomechanical properties of the polymer was observed upon irradiation at these temperatures [13] and, more recently [13, 14] presumed the cross-linking of the polymer chains of polytetrafluoroethylene, when irradiated at temperatures above its melting point. This presumption was based on indirect data concerning decreases in the strength and breaking elongation, increases in the modulus of elasticity and the limit of fluidity, and decreases in the size of the crystallites and degree of crystallinity. Such behavior is typical of polyethylene and other polymers for which the radiation-chemical cross-linking of the polymer chains is a fairly reliably established fact. Hence, the conclusion about cross-linking of the polytetrafluoroethylene macromolecules, made by Abramova et al. [13, 14], is valid to the extent to which the behavior of this polymer can be regarded analogous to that of different polymers. Cross-linking in polytetrafluoroethylene cannot be proved directly, e.g., based on the solubility data, because of its absolute inertness to all solvents.

In the recent decade, the interest in radiation exposure of polytetrafluoroethylene in melt has increased, and relevant research activities have been undertaken in Japan [15–20] and Germany [21–24].

Oshima, et al. [15] showed that radiation exposure of polytetrafluoroethylene in an oxygen-free medium at temperatures higher than the melting point of the crystallites (327°C) causes the modulus of elasticity, the limit of fluidity, and the radiation resistance to increase (this method for radiation-induced modification of polytetrafluoroethylene was patented in the US [16]). In this method, of principal importance is irradiation of the samples in a medium free from molecular oxygen. It is a well known fact that, in the presence of oxygen, the radiation-chemical yield of polytetrafluoroethylene chain degradation tends to increase. This makes the lack of oxygen a fully justified requirement for high-temperature radiation exposure experiments, the more so that this method is underlain by the concept of radiation-chemical cross-linking of polytetrafluoroethylene, which process is directly opposite to degradation of the polymer. Another distinctive feature of the method proposed is that only film samples (no thicker than 500 μm) were modified, and block samples were not involved.

Experiments on electron beam exposure of films typically utilize electron accelerators, which create high electron flux densities and, thereby, high absorbed dose rates. However, this poses limitations on the thickness of the modified layer of the material, associated with the limited pathway of electrons in a substance. Treatment of materials having a characteristic thickness of 10 mm and over requires g-radiation with a high penetrating ability, which provides for uniform distribution of the properties in the bulk of the modified item. In turn, g-ray sources find only limited use because of low radiation intensities and the ensuing low absorbed dose rates. For typical g-ray sources (^{60}Co , average quantum energy 1.25 MeV) the dose rate is 2–3 orders of magnitude lower (typically, 1–10 kGy h^{-1}) than in the case of electron accelerators. Therefore, at not very high radiation-induced modification efficiencies, which requires large absorbed doses, the use of g-ray sources entails too high expenses because of the need in prolonged maintaining of the appropriate process modes.

Katoh et al. [19] reported that, at 1000 kGy, the yield of molecular cross links is low, 0.2/100 eV, and

tends to decrease with decreasing dose (at 500 kGy, no cross links were found!). Those data suggest that g-radiation exposure is inexpedient for radiation-chemical cross-linking of polytetrafluoroethylene in melt, and the corresponding procedure of modification of block items is unpromising. This specifically stimulated the German and Japanese researchers' interest in films and the use of electron accelerators suitable for systematic studies of the process over a wide range of absorbed doses, 500–10000 kGy, which are virtually unattainable with g-rays.

At the same time, the whole body of information on the structure of polytetrafluoroethylene irradiated in melt, derived in the above-mentioned studies with the use of ^{13}C and ^{19}F NMR, as well as IR spectroscopy, combined with the differential scanning calorimetric, thermogravimetric, and physicomechanical data [15–24], does not suggest unambiguously cross linking of the polymer chains in polytetrafluoroethylene. For example, the presence of the side $-\text{CF}_2$ group [19], consistent with the T-type cross linking, can be explained by formation of C_2F_5 and C_3F_7 branches. The above-mentioned studies were focused on fluoromethyl branches only [17–24], but radiolysis of polytetrafluoroethylene yields not only CF_3 but also C_2F_5 and more extended radicals capable of recombination with the radicals in the middle of the main chain to form side branches. Clearly, the presence of tertiary carbon atoms ($-\text{CF}<$) in the main chain also does not prove cross linking, since it can be explained by the presence of the same side branches.

We developed a method for radiation-induced structural modification of polytetrafluoroethylene, which afforded unprecedented improvement in the quality of the material: The wear resistance increased by a factor of 10^4 , and the creepage decreased by a factor of 10^2 [25]. The principal feature peculiar of this method is that the polymer is treated by penetrating rays at temperatures exceeding the melting point of polytetrafluoroethylene in a gas medium containing the impurity molecular oxygen at relatively low absorbed doses (no greater than 200 kGy). The underlying concept of this method is that modification of the macroscopic properties of polytetrafluoroethylene is driven predominantly by accumulation of radiation-induced defects in the crystalline phase. The benefits associated with the method recommended for radiation exposure of polytetrafluoroethylene in melt [25] include: (1) suitability not only for films but also for block polymer items; (2) no need in fillers and low-

molecular-weight hydrocarbon sensitizers; (3) substantial increase in wear resistance and decrease in creepage at doses attainable with g-ray sources (much lower than 500 kGy); and (4) uniform spread of the properties in the polymer bulk.

Structural and Morphological Characteristics of Radiation-Modified Polytetrafluoroethylene

Modern technology implies the use of emulsion and suspension polymerization for preparation of polytetrafluoroethylene as a powder with different dispersities to be further used for manufacturing block items (cores, cartridges, disks, etc.) by powder metallurgy methods. The degree of crystallinity of the powder particles is 95–98%. The powder is subjected to cold pressing in press molds and then sintered at 380°C. This specific procedure is applied because the polytetrafluoroethylene melt has a very high viscosity (10^{11} – 10^{12} Pa s) and is unable of flow. The enthalpy of melting is low, which, along with a high melting point, suggests a low entropy of the process. It is believed that, in the molten state at temperatures within 327–420°C, the former crystallite domains preserve their ordering to a certain extent and form a meso phase, initially of a smectic, and, with increasing temperature, of a nematic type. Above 420°C, polytetrafluoroethylene is depolymerized with the monomer eliminated.

Thus, heat treatment of pressed blocks at 380°C does not cause melting of crystallites in the conventional sense of this word. Rather, specifically sintering (“pasting”) of the surfaces of the crystallites due to their partial amorphization (disordering) is observed. The crystalline core of the powder particles remains unchanged throughout the process (pressing, sintering, cooling).

The supramolecular structure of block samples of polytetrafluoroethylene, “frozen” after sintering, is comprised of extended polymer chains forming long crystallites (stacks) consisting primarily of the through chains and disordered amorphous phase interlayers. The X-ray crystallinity of standard samples is typically 75%. The amorphous phase of the polymer remains partly ordered due to a high degree of chain orientation, by contrast to flexible-chain hydrocarbon polymers whose chains in the amorphous phase tend to a coiled configuration.

Another morphological feature of the polytetrafluoroethylene structure is porosity. Application of the

powder metallurgy technology for preparation of polytetrafluoroethylene blocks poses rigid requirements on the quality of the powder (cleanliness, dispersity, molecular weight) and on the pressing and sintering modes. Clearly, ideally homogeneous blocks cannot be prepared in practice. Real block fluoroplastic-4 is a fairly porous body (1–2%), whose porosity type varies with the item (core, cartridge, plate, tube, etc.), as well as with the pressing technique (vertical, horizontal, isostatic, extrusion) and the geometric size and brand of the powder used. Deviations from the process modes (e.g., mixing powders with different dispersities, presence of catalyst residues and other impurities, noncompliance with the pressing or sintering conditions) cause additional increase in porosity of the material, culminating in formation of macroscopic extended areas having a “loose” structure with the porosity of up to 5% or over.

Below, we will discuss the experimental results that allow certain conclusions about the nature of the changes in the macroscopic properties of polytetrafluoroethylene due to radiation exposures at temperatures above the melting point of crystallites and in the presence of an oxygen impurity.

Figure 1 shows the data on wear resistance of the radiation-modified polymer sample. The wear intensity for the best polytetrafluoroethylene-based compositions in identical tests was estimated at 1–2 mg h^{−1}. The wear resistance of the irradiated sample (200 kGy dose) at molecular oxygen pressures within 10^{−2}–1 mm Hg is lower. At pressures close to 10^{−1} mm Hg the best result

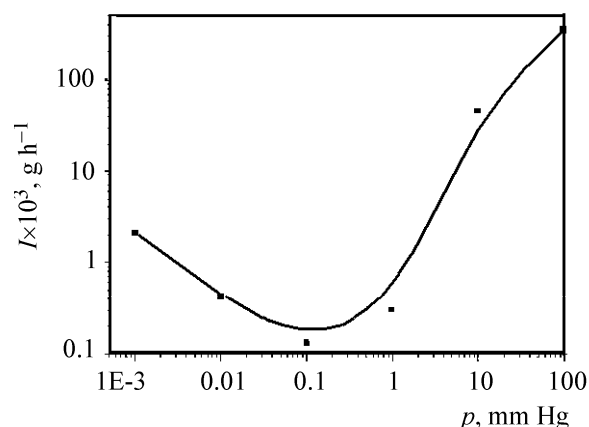


Fig. 1. Average mass wear intensity of block samples of modified polytetrafluoroethylene vs. oxygen pressure in the reaction chamber. Absorbed dose 200 kGy. Kinematic test scheme: pin-on-disk, load 2.5 MPa, sliding rate 1 m s^{−1}, friction path 10000–15000 m.

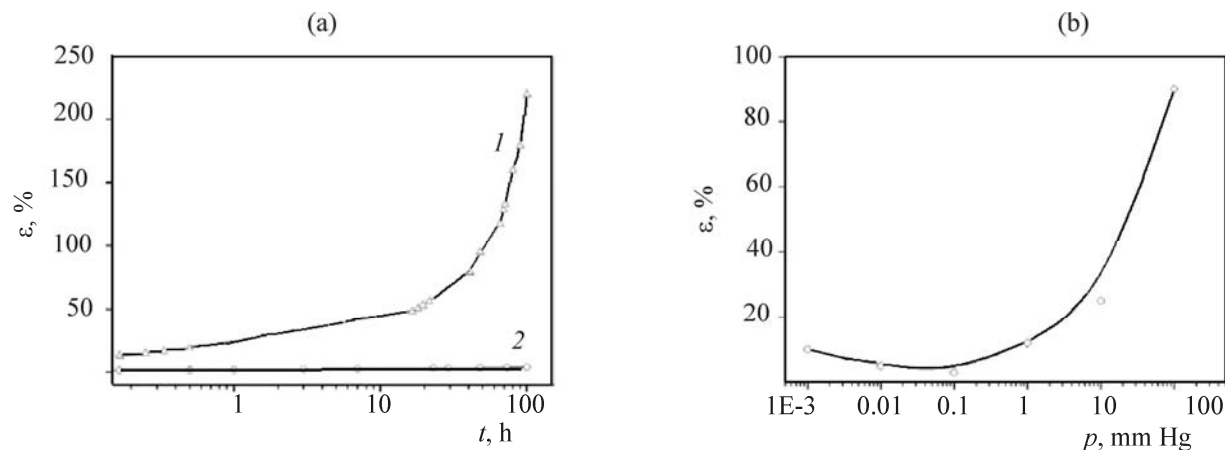


Fig. 2. Variation of strain (a) with time for (1) initial and (2) modified polytetrafluoroethylene film in the creep mode and (b) with oxygen pressure in the reaction chamber for modified film. Film thickness 100 μm , test portion width and length 5 and 20 mm, respectively; load 11 MPa; working temperature 18–20°C. Modification conditions: absorbed dose 200 kGy; oxygen pressure 10^{-1} mm Hg.

is achieved: a wear resistance exceeding 10^4 times that of the initial polymer, and 10–20 times, that of composite materials. In the same pressure range, the creepage of the modified polymer is at a minimum: by a factor of 20–100 lower than that of the initial material (Fig. 2).

These data suggest that a fairly weak, from the radiation chemistry viewpoint, exposure (200 kGy) causes abnormally strong changes in the macroscopic properties, wear resistance, and creepage.

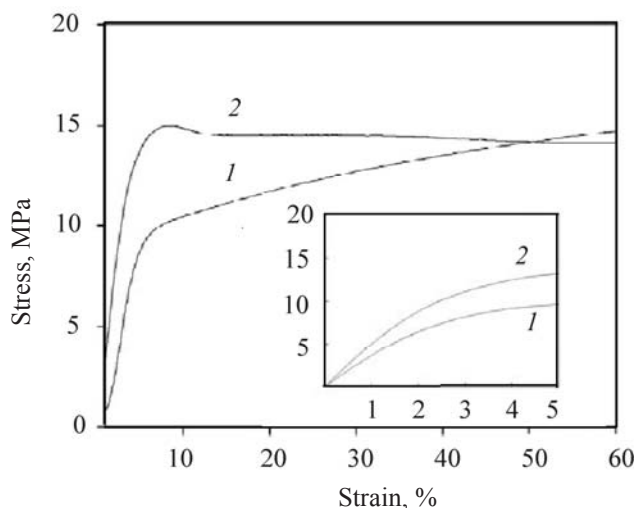


Fig. 3. Stress–strain curves for (1) initial and (2) radiation-modified polytetrafluoroethylene. Insert: stress–strain curves in the region of low strains. Absorbed dose 200 kGy; oxygen pressure in the reaction chamber 10^{-1} mm Hg.

Figure 3 shows the stress–strain curves for the initial and irradiated polytetrafluoroethylene samples. The initial material has two basic characteristic features. First, irreversible plastic strain makes a significant contribution already in the initial stage of application of the mechanical load. A linear segment of the curve corresponding to elastic strain is not recorded at all. In the case of other polymers (e.g., polyethylene, polypropylene, F-40) this segment is clearly manifested and interpreted as due to relaxation-induced modification of the polymer chain configuration in the direction of the mechanical load applied. Upon attainment of the induced elasticity limit (with increasing mechanical load) the linear segment corresponding to elastic strain is typically replaced by plastic strain (flow) segment. Nonlinear response of polytetrafluoroethylene in low strain region can be easily understood, considering the morphological characteristics of its structure, i.e., high degrees of crystallinity, high degree of chain orientation in the amorphous phase, and linear chain configuration, combined with a low shearing strength of the crystallites. These factors give rise to cold flow, which is not characteristic for other polymers and is manifested in development of irreversible plastic strain already in the initial segment of the stress–strain diagrams. Such pattern is responsible for the second characteristic: structurally and morphologically uniform elongation of the sample in the entire test portion without necking till the sample ultimately fails (Fig. 3, curve 1).

The run of the stress–strain curves for the irradiated polytetrafluoroethylene in low-strain region is similar

to that for the initial sample (Fig. 3, curve 2 in insert). However, a peak corresponding to the induced elasticity limit and transition to a viscous flow state appears in the strain–stress diagram (Fig. 3, curve 2). In this area, the strains in irradiated polymer sample are characterized by necking.

These results suggest that the radiation exposure of polytetrafluoroethylene in melt causes an increase in the degree of intermolecular bonding of polymer chains. One reason to this can be found in cross linking of the polymer chains. However, as mentioned above, the presence of cross links in polytetrafluoroethylene has not been unambiguously proven experimentally and, also, the factors responsible for the fact that, upon passing through the melting point, the path of the radiation-chemical processes changes to the opposite, from degradation to cross linking, still remain to be elucidated. There are no published data to provide explanations to this phenomenon.

At the same time, stronger intermolecular bonding in irradiated polytetrafluoroethylene can be explained in a different way, as due to arising and increasing disorder in the system, associated with formation and accumulation of radiation-induced defects. Considering the specific structural features of this polymer, the radiation-induced defects in the crystalline and amorphous phases should affect substantially the supramolecular structure and strain properties.

The major defects caused by radiation exposure of polytetrafluoroethylene in an oxygen-free atmosphere are terminal ($\text{CF}_2\text{--CF}_2\text{--}$) and middle ($\text{--CF}_2\text{--}\dot{\text{C}}\text{F--CF}_2\text{--}$) fluoroalkyl macroradicals. In the presence of molecular oxygen, terminal ($\text{--CF}_2\text{--CFOO}\cdot$) and middle ($\text{--CF}_2\text{--CFOO--CF}_2\text{--}$) peroxide macroradicals are formed in a nearly 1:1 ratio of yields [26]. Thermal degradation of fluoroalkyl and peroxide radicals at temperatures above 100°C yields terminal double bonds (--CF=CF_2), terminal --CF_3 and --CFO groups, free radicals ($\text{CF}_3\cdot$, $\text{C}_2\text{F}_5\cdot$, $\text{C}_3\text{F}_7\cdot$), neutral products CF_2O , CO , CO_2 , and perfluoroalkenes. An oxygen impurity causes overall increase in the amount of radiolysis products, including radiation-induced defects in the main chain (terminal groups, double bonds, etc.).

There exist reliable evidence of formation of chain branchings (--CF<), side branches >CF--CF_3 and $\text{>CF--C}_2\text{F}_5$, terminal --CFO groups, and double bonds (--FC=CF-- , --CF=CF_2) upon radiation exposure of polytetrafluoroethylene at temperatures above the

melting point, as well as of a significant increase in the concentration of terminal --CF_3 groups [19, 21–23], associated with scission of the main chains of the polymer. All these products, except for chain branchings and side branches, are yielded by radiolysis of polytetrafluoroethylene at room temperature as well, which suggests proceeding of similar radiation-chemical processes. At the same time, by contrast to the polymer at low temperatures, in the molten state low-molecular-weight products acquire a considerably higher diffusion mobility and ability to migrate over the polymer bulk, including former crystallite areas. This increases the probability of secondary reactions of these products with middle macroradicals to yield side branches.

The radiation-chemical yield of branches is determined by competition of three processes: (1) thermal degradation of fluoroalkyl macroradicals; (2) reaction of fluoroalkyl macroradicals with molecular oxygen to form peroxide macroradicals, followed by thermal degradation of the latter; and (3) recombination of fluoroalkyl macroradicals with low-molecular-weight free radicals. The first-named process dominates in the absence of oxygen, at a not very high total content of radiolysis products, and second-named process, under oxygen excess. In the intermediate case recombination of fluoroalkyl macroradicals with free radicals should make a greater contribution. In this radiation-chemical scenario, the presence of impurity molecular oxygen is of principal importance and increases the yield of side branches due to overall increase in the amount of the radiolysis products.

An important feature of the radiation-chemical transformations considered is that, above the melting point, they proceed homogeneously in the polymer bulk, i.e., not only in the amorphous phase but also in the ordered meso phase. This directly follows from the fact that, despite high viscosity, the gas permeability of polytetrafluoroethylene tends to sharply increase near and above the melting point. This is responsible for formation of the above-mentioned radiation-induced defects (terminal groups, side branches, double bonds) in the former crystallite areas, so that the crystal structure of the polymer is disturbed during subsequent cooling.

Also, we revealed another type of radiation-induced defects associated with radiation exposure of polytetrafluoroethylene in melt. [27]. These are conjugated π -bonds whose existence is unambiguously suggested by the fluorescence ability in the visible, exhibited by the

irradiated polymer. The initial polymer does not exhibit absorption at 200–800 nm and also is not able of fluorescence upon UV-excitation at 200–400 nm. The modified polytetrafluoroethylene exhibits bright fluorescence in the visible (Fig. 4), which sharply decays upon radiation exposure at pressures above 1 and under 10^{-2} mm Hg.

The fluorescence centers in modified polytetrafluoroethylene are represented by polyene moieties containing conjugated double bonds in various numbers. These moieties do not exhibit phosphorescence upon cooling the samples to 77 K, which is a characteristic feature of conjugated chain moieties $-(CF=CF)_n-$. Cyclic moieties comprising a π -system exhibit both fluorescence and phosphorescence [28]. The absorption band maxima of polyenes are shifted to longer waves with increasing number n [29]. Appropriate calculations show that fluoropolyenes in the polymer chain of the modified polytetrafluoroethylene are characterized by $n = 4-7$. Presuming that the absorption coefficient for them is close to those for alkylpolyenes, i.e., $80000-140000 \text{ l mol}^{-1} \text{ cm}^{-1}$, the concentration and radiation-chemical yield of fluoropolyenes can be estimated at $(1-5) \times 10^{18} \text{ cm}^{-3}$ and $(0.1-0.5)/100 \text{ eV}$, respectively. To our knowledge, this is the first case of detecting and providing direct evidence of formation of polyenes in polytetrafluoroethylene.

The relative content of the conjugated moieties in the modified polytetrafluoroethylene does not exceed 0.1% and thus cannot substantially affect its chemical resistance, as well as dielectric and other characteristics. The concentration of radiation-induced defects

of different kinds is 0.1–1.0%, as follows from typical values of radiation-chemical yields.

The considered radiation-chemical defects cause the polymer chain rigidity to decrease, and the conformation mobility (flexibility), to increase; they weaken the intermolecular repulsion and interfere with mutual sliding of chains. The defects, “frozen” after irradiation in the crystalline phase, are responsible for “loosening” of the crystalline core of the particles, decrease in the size of crystallites, and increase in the shearing strength of the crystallites. All this leads to formation of physical engagements of the kinetic segments of the macromolecules (“entanglement” of the macromolecules), homogenization of the supramolecular structures, and decrease in porosity.

Formation of radiation-induced defects in that low concentration (no higher than 1%) cannot in itself substantially affect the macroscopic properties, but, as follows from the analysis above, can be responsible for intensify their influence on the mechanical properties (wear resistance and creepage) due to the change in the crystallinity, as well as in the size and defectiveness of the crystallites. By contrast to flexible-chain polymers, quenching (fast cooling from melt) of polytetrafluoroethylene, which causes the crystallinity to decrease by 10–20%, appreciably improves its viscoelastic properties. In this respect, polytetrafluoroethylene exhibits a trend opposite to that typical for other polymers whose mechanical properties are deteriorated by a decrease in crystallinity.

The X-ray examinations showed that, upon exposure of polytetrafluoroethylene in melt at a dose of 200 kGy, the degree of crystallinity increases by 7% (an increase in crystallinity at low doses is consistent with the earlier reported results; see, e.g., [16]), but the average size of the crystallites substantially decreases (by more than half across). This is responsible for increase in the optical transparency of the samples: The initial sample is white because of diffuse light scattering on crystallites, and the modified sample in a thin layer is virtually transparent and does not scatter light (Fig. 5). An increase in crystallinity is associated with the known effect of exhaustive crystallization of polytetrafluoroethylene in the amorphous phase because of degradation of the polymer chains, which facilitates structural relaxation. A decrease in the average size of the crystallites is due to accumulation of crystal defects.

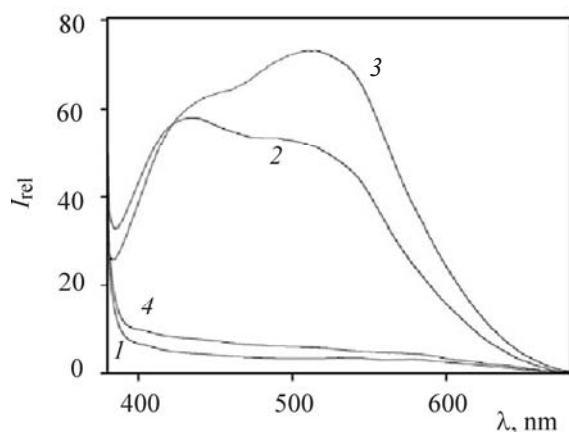


Fig. 4. Fluorescence spectra of modified polytetrafluoroethylene under excitation at $\lambda = 365 \text{ nm}$. Absorbed dose 200 kGy, and oxygen pressure, mm Hg: (1) 10^{-3} , (2) 10^{-1} , (3) 1, and (4) 100.

Thus, taken together, the above-described physico-chemical processes induced by radiation exposure of polytetrafluoroethylene in melt substantially modify the supramolecular structure of the amorphous and crystalline areas in polytetrafluoroethylene. Considering the specific interrelation of the supramolecular structure and macroscopic properties of polytetrafluoroethylene, this suggests a structural-morphological nature of the unusual radiation-induced effects revealed for the polymer melt.

Main Performance Characteristics and Applications Radiation-Modified Polytetrafluoroethylene

Radiation-modified polytetrafluoroethylene was used for preparing an antifriction and sealing material having much better characteristics compared to the initial polymer and its compositions. These include higher (up to 10^4 times) wear resistance and 100–150 times lower compressive and tensile creep, and several times higher optical transparency in the visible. The dielectric characteristics and friction coefficient are preserved at the level typical for the initial material. Also, because of a low concentration of radiolysis products (radiation-induced defects), these materials preserve such important properties as chemical, biological, and thermal stability.

The major comparative characteristics of the initial and radiation-modified polytetrafluoroethylene are listed in the table.

The new material holds much promise for applications in industries that traditionally utilize polytetrafluoroethylene. The set of properties of the radiation-modified polymer combining the initial and imparted characteristics provides for substantial increase in the service life of those items where polytetrafluoroethylene is already used, and allows solving materials science problems in fields where its application has been impossible so far.

At the present time, ordinary (unmodified) polytetrafluoroethylene is extensively applied in sealing elements of pistons in lubrication-free compressors and sealing parts of hydro and pneumatic cylinders of ball valves on main and industrial oil and gas pipelines, etc. The set of above-listed properties of the radiation-modified polytetrafluoroethylene developed by us will sharply increase the robustness and service life of these items.

A new promising line in application of radiation-modified polytetrafluoroethylene in aviation engineer-

ing can be found in development of a high-temperature sealing material for pneumatic, hydro, and fuel systems operated at a working pressure of 28 MPa and a temperature of up to 200°C. This problem still remains to be solved.

As regards development of materials intended for engineering and technical, as well as hygienic and medical applications, radiation-modified polytetrafluoroethylene holds promise for manufacturing membranes and filters exploited in aggressive liquid and gaseous media. The advantages of the material proposed over the currently used materials are associated with better characteristics from among the set of the above-mentioned properties.

It is expected that increase in the radiation resistance will significantly extend the application field for polytetrafluoroethylene. This will make it suitable for space engineering application, namely, in manufacture of thermal control coatings of the solar reflector class, friction units, and onboard cable insulation on outer surfaces of space vehicles. In many cases modified polytetrafluoroethylene will be preferred over currently used F-4MB (a tetrafluoroethylene-hexafluoropropylene copolymer), polyvinyl chloride, polyethylene terephthalate, and polyamide.

In nuclear power engineering the use of radiation-modified polytetrafluoroethylene will allow solving a topical problem of development of a sealing element for the cooling circuits of nuclear reactors. At the present time, copper seals are used for these purposes but do not provide adequate sealing for prolonged time, which results in leaks. Graphite seals recommended for use at the present time surpass copper seals

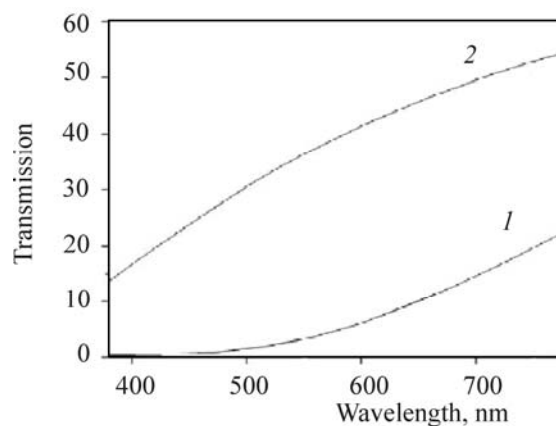


Fig. 5. Transmission spectrum of (1) initial and (2) radiation-modified film (thickness 100 μm). Absorbed dose 200 kGy; oxygen pressure 10^{-1} mm Hg.

Comparative characterization of the initial and radiation-modified fluoroplastic-4

Parameter	Initial sample	Modified sample
Friction coefficient in the pin-on-disk kinematic scheme	0.06–0.08	0.06–0.08
Wear in the pin-on-disk kinematic scheme at a load of 25 kg cm ⁻² and sliding rate of 1 m s ⁻¹ , mg h ⁻¹	800–1000	0.03–0.15
Tensile strength, MPa	25–30	14–18
Breaking elongation, %	350–450	100–250
Tensile modulus, MPa	280–350	300–400
Compressive modulus, MPa	450–500	560–740
Stress at 10% strain, MPa	15	25
Induced elasticity limit, MPa	Fluidity in the region of low strains and loads	≥14
Creepage at room temperature at a static load of 70% of the tensile strength in 100 h, %	150	≤5
Compressive strain (14 MPa load) in 24 h, %	16	≤10
Proportion of irreversible strain in compression 24 h after removal of load (14 MPa), %	75	≤1
Dielectric permittivity at 10 ⁹ Hz	2.1	2.1–2.2
Dielectric loss at 10 ⁹ Hz	2.0×10 ⁻⁴	(2.0–3.0)×10 ⁻⁴
Optical transmission of the 100-μm film at 400–800 nm, %	≤25	≤60
Exploitation temperature, °C	250	250
Chemical stability	High	Unchanged
Gas evolution [GOST (State Standard) R 50109], %	<0.01	Unchanged
Radiation resistance, Mrad	1	100–300

in the service life, but rank below polytetrafluoroethylene in the mechanical properties providing for high-quality sealing.

Radiation-modified polytetrafluoroethylene can be applied in manufacturing sliding bearings (e.g., ball bearings of suspensions in cars) and medical items. Especially topical is application, so far impossible, of the new material in medical items subjected to radiation sterilization.

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