

# Accumulation of free radicals in irradiated Polytetrafluoroethylene and study of its properties

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**Abstract.** The accumulation of free radicals in polytetrafluoroethylene (PTFE) is experimentally studied and its properties are investigated by ESR, Raman spectroscopy and optical microscopy.

## 1. Introduction

At present, the question of the effect of ionizing radiation on the dielectric systems seriously arises in connection with their wide use in space technology, nuclear industry and nuclear power.

The necessity of such studies is due to clarify the behavior of polymeric materials working in the fields of different streams of particles. Data in the literature give a large spread in the results, since the radiation resistance of dielectric solids can depend strongly on the specific conditions of their production and testing (type of radiation, exposure mode - continuous or pulsed, short or long, in air or vacuum, at different dose rates in during the tests, etc.). In particular, the effects of radiation oxidation in the air may result in greater damages even at low dose rates with fixed integral doses.

When electron and gamma-irradiation (electromagnetic impact) in the polymers the rupture of the bonds and cross-linking of the polymer occurs. In practically all polymers and composites with increasing radiation dose occurs deterioration of mechanical strength (predominates radiation degradation), except for polyimide (in which at not very high doses the predominance of cross-linking over degradation is observed).

Most of the reactions and effects in this case are irreversible [1 – 2]. In the interaction of electrons with polymers the following processes occur: 1. The scattering of incident particles by electrons of atoms. At the same time there goes or excitation of an atom or its ionization. In this process, about 99% of primary energy is lost by a charged particle. These so-called ionization losses. In the polymer when ionization the polymer chains are scissioned, from which free radicals, volatile substances (degradation) are appeared. A significant part of scissioned bonds of atoms reacts with the nearest neighbors, forming stable compounds (cross-linking). The charged particles depending on the energy can produce from a few dozen to several thousand collisions. Ultimately, the particle is stopped, forming a profile of defects, of scissioned bonds and radiation damages. In this case, almost all the physico-chemical properties are substantially changed. 2. Scattering of the primary particles by atoms. In this case knocking of the atom as a whole occurs and the so-called primary- knocked atom (PKA) is formed. PKA generates secondary, tertiary knocked atoms, etc. and atom-atomic cascade arises. The cascading areas are formed from which the vacancy clusters and clusters of interstitial atoms are finally formed. The mechanism of defects generation during gamma irradiation is about the same as in the electron irradiation. However, the effectiveness of gamma-irradiation (per unit volume of material) is approximately 100 times smaller than for electron impact. When considering of the single trajectories, the process of passage of electrons can be considered as chaotic and for a finding of any physical quantity it is necessary to gain a large number of measurements. After a lot of trials and averaging



over the angles, energies and the depths of a physical quantity (streams of particles, the concentration of defects, etc.) are reduced to a minimum scatters and errors.

The difficulties arising when interpreting experimental data are primarily associated with the development of an adequate model, by the complexity of the mathematical description of the phenomena, incomplete informativeness of methods and lack in practice of the net materials. The presence of defects or accelerates or slows down the processes (especially diffusional) in the tens or hundreds of times. Naturally, this is affected and on the end result – the formation of different compounds and structures and on the physical properties of the material. [1 – 3].

### Experimental technique

The industrial Teflon – 4 was used. The irradiation of material samples was conducted by electrons in air at room temperature on a accelerator of quasi-continuous action ELU–6 under the following beam parameters: 1. Energy – 2 MeV. 2. The current density  $j = 0, 5$  mA. 3. The sample temperature was 273K. The irradiation by gamma rays was conducted on the installation Co<sup>60</sup>. The samples were represented themselves as a packing from the Teflon film and 2 cylinders with a diameter of 2.5 mm and a length of 5 mm and a mass of ~ 62 mg. The irradiation was conducted in a thermal bath at temperatures 273 K, after which the samples were stored in liquid nitrogen. The annealing was held at room temperature ( $T = 293$  K). Isotopes in the form of cylinders were located along the azimuth around the target in order to obtain uniform treatment.

ESR spectra were measured with a spectrometer ESP 300E, which is designed to study paramagnetic centers and their identifications. The essence of ESR lies in resonance absorption of radiofrequency power with redundant number of unpaired electrons in the samples that are in a constant magnetic field. Raman spectrometer of the system NTMD INTEGRA SPECTRA was used for the study of the Raman spectra. The modular structure of the spectrometer, a wide range of lasers and microscopes, the use of automatic three-position elements for operations with three lasers, the availability of switching or simultaneous use of three lasers with automatic tuning of optical and mechanical elements for obtaining maximum efficiency of the work makes the system flexible and allows us to solve a large number of tasks. The main technical characteristics of the Raman spectrometer: 1. The working wavelength range is 244 – 1050 nm. 2. Diffraction gratings depend on the configuration. 3. The spectral resolution is 0.1 Å. 4. Focal length is 520 mm.

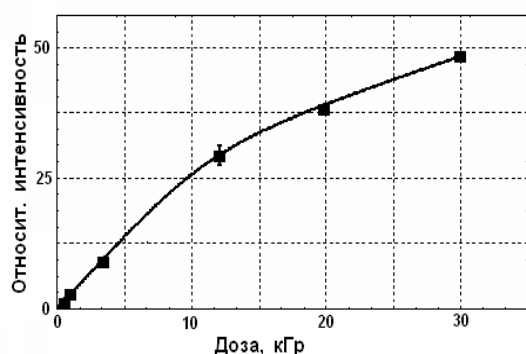
The study of the surface structure was carried out at the optical microscope Leica DM 6000M, which is a system with a high-resolution digital cameras and software for analyzing and storing images. The device has the following features and options: 1. Automatic mode of the incident light (reflection) for the methods of light and dark field. 2. Automated mode of the transmitted light (on clearance). 3. Automated dimmers, changes of the aperture and aperture of the illuminator. 4. Motorized drive focus and a motorized objective little table responsible for x, y and z movements. 5. x / y panel motorized stepping motor, the removable objective little table with external dimensions: 234 x157 mm, the traverse range: 76 x50 mm, the minimum step: 0.3 µm, z panel corresponds to removable plate, the traverse range – 25 mm, the minimum step – 0.015µm, the maximum speed –5 mm / s, the minimum speed – 1mm / s, the maximum load – 4 kg. 6. Motorized, encoded turret head with 6 lens with magnification 5x, 10x, 20x, 50x, 100x, 150 x times. 7. The unique memory function for simultaneous switching of the lens and the contrast method. Color selection of image (for detection of small or subtle elements of the sample in contrast).

### Experimental results

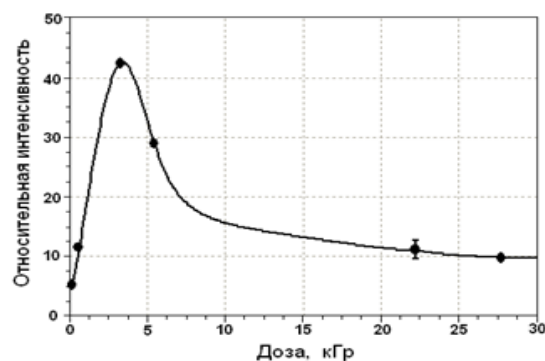
The intensity of the ESR signal in Polytetrafluoroethylene on the dose of  $\gamma$ -irradiation <sup>60</sup>Co at 273 K is shown in Figure 1. As can be seen from the figure, with an increase in irradiation dose the signal intensity increases and gradually reaches saturation, indicating an increase in the number of free radicals.

Figure 2 is shown the dependence of the accumulation curve of the concentration of radicals on the absorbed dose of radiation at a temperature of 333 K. As shown in Figure 2, the radical concentration initially increases in proportion to the dose, reaches a maximum and then decreases exponentially.

The curve of the intensity depending on the irradiation dose can be explained. Such move of depending is explained by the competing processes of accumulation and radical loss, the mobility of which increases with increasing temperature.



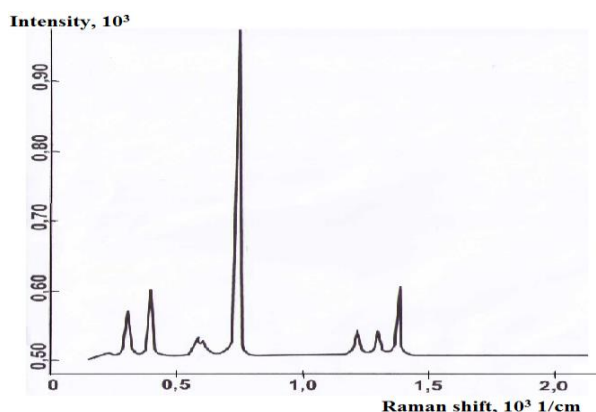
**Figure 1.** The dependence of the intensity of the ESR signal in Polytetrafluoroethylene on the irradiation dose at 273K



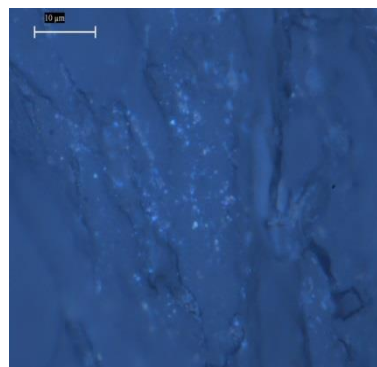
**Figure 2.** The dependence of the intensity of the EPR signal in PTFE on the dose of  $\gamma$ -irradiation  $^{60}\text{Co}$  at 333 K

Further Raman spectra of unirradiated and irradiated PTFE were measured. Figure 3 shows the Raman spectrum of the irradiated PTFE with a dose of 13.5 kGy (film thickness was  $d = 40$  micrometers). There are seven precisely expressed peaks. For irradiated materials in comparison with unirradiated the frequencies are slightly changed.

The intensity of the peaks in the spectrum after irradiation of Polytetrafluoroethylene films are significantly increased (more than 2 times), which is associated with changes in the structure of the material. This is confirmed by optical studies. The changes of bands in the spectrum are associated with a very quick and active reaction of transition of primary fluoroalkyl radical  $\sim \text{CF}_2 - \dot{\text{C}}\text{F}_2 - \text{CF}_2 \sim$  into the peroxygen radical  $\sim \text{CF}_2 - \text{CF}(\text{OO}\cdot) - \text{CF}_2 \sim$  which is due to oxygen is always present in the polymer matrix.



**Figure 3.** Raman spectrum of the irradiated PTFE with a dose of 13.5 kGy



**Figure 4.** The image of fluoroplastic film surface after irradiation with a dose of 13.5 kGy. Field of view is 44 x 33 mm

The study surfaces of unirradiated PTFE films when viewing specimens on a gleam in an optical microscope shows that most part of surface of the samples are homogeneous, smooth surface and looks as matte blue. After irradiation with a dose of  $D = 13.5$  kGy it can be seen that the materials have completely inhomogeneous surface with varying degrees of transmission. In addition, dark and light spots of different densities ranging in size from one to several micrometers with clear boundaries for their localization (Figure 4) are seen.

### Findings

1. The experimental studies of ESR spectra in Polytetrafluoroethylene irradiated by gamma rays at 273 K are carried out. It was found that the introduction of radiation defects significantly increases the intensity of the signal amplitude. With increasing irradiation dose the signal intensity increases and gradually reaches saturation, indicating an increase in the number of free radicals. At a temperature of 333 K on the curve has a pronounced maximum. Such move of depending is explained by competing processes of accumulation and radical loss, the mobility increases with increasing temperature.
2. The experiments show that Raman spectra of the irradiated (and unirradiated) PTFE have seven precisely expressed peaks. Their intensity after irradiation are significantly increased (more than 2 times) which is associated with changes in the structure of the material. The bands changes in the spectrum are associated with a very quick and active reaction of transition of primary fluoroalkyl radical  $\sim \text{CF}_2 - \dot{\text{C}}\text{F}_2 - \text{CF}_2 \sim$  into the peroxygen radical  $\sim \text{CF}_2 - \text{CF}(\text{OO}^\cdot) - \text{CF}_2 \sim$  which is also due to oxygen is always present in the polymer matrix.
3. The surface of the unirradiated PTFE films when viewing specimens on a gleam in the optical microscope shows that most of it is a homogeneous, smooth surface. The irradiation leads to inhomogeneity of the surface with varying degrees of transmission. The dark and light spots of different densities ranging from one to several microns with clear boundaries of the regions of their localization are observed.

### References

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