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Mechanical and Optical Properties of Polytetrafluoroethylene Treated by γ -Irradiation near the Melting Point

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Radiation-modified polytetrafluoroethylene (PTFE), which exhibits intense fluorescence in the visible spectral region, was prepared. Radiation modification was performed with ⁶⁰Co rays at 330 °C, at a dose of 0.2 MGy. The mechanical properties, fluorescence and electronic absorption spectra of film and block PTFE specimens irradiated under the given conditions were studied.

Keywords: Polytetrafluoroethylene; Gamma-irradiation, Modification, Degradation.

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The problems of modification of PTFE [1, 2] and other polymers by radiation treatment in melting state were studied by a number of researchers. Some abnormal phenomena related to the changes in macroscopic properties of PTFE after irradiation under vacuum at the temperature higher, than PTFE melting point, as well as in the presence of molecular oxygen have been found [3]. In the works [4], was established that irradiation of PTFE under such conditions leads to an increase in the modulus of elasticity, yield strength and resistance to radiation compared to the original material. Recently, it was found that subjected to γ -irradiation PTFE near the melting point possesses color and fluorescence [5 - 8].

The aims of the resent work appear as follows:

- to investigate the effect of irradiation conditions on some mechanical properties of the modified PTFE.
- to clear up relationship between fluorescence properties, coloring, and absorbed doses of γ -irradiation;
- to characterize the distribution of the formed optical centers over the bulk of the sample (only for block samples);
- to give a spectral characterization of the absorbance and fluorescence of that centers.

I. Experimental

The industrial standard PTFE (F-4 EO), density $\rho = 2,20 \text{ g/cm}^3$, molecular weight: $M = (5 \pm 10) \cdot 10^6$, was used in our experiments as a base material for specimens preparation. The samples of thin polymer films 20×20 mm with thickness 100 μm and polymer blocks

50×20×20 mm sizes was analyzed.

It is known, that the presence of oxygen admixture has a substantial effect on a radiation-chemical processes in polymers, and especially this influence is pronounced in PTFE. In order to estimate the effect of presence of oxygen at irradiation procedure on resulted product, a series of film samples with different oxygen content was prepared. Initially, for elimination of molecular oxygen impurities that originally was entrapped in the bulk of specimens, the films (samples 1 – 4) were (additionally) outgassed at ambient temperature in a vacuum Pirex capsules (VPC) with residual pressure (10^{-3} mm Hg for 2 hours). Then atmospheric purified air was admitted to the VPC with samples 2, 3 and 4 at pressure 10^{-1} , 1 and 100 mm Hg, respectively with subsequent VPC encapsulation. To have lowest possible concentration of molecular oxygen in the film specimen, the sample 5 was outgassed in VPC at 380°C under dynamic vacuum with residual pressure 10^{-3} mm Hg for 2 hours and immediately encapsulated.

Irradiation of encapsulated film and not treated block of PTFE specimens was carried out by γ -rays from a ⁶⁰Co source in temperature stabilized chamber at 330 °C. Before the irradiation procedure, the vacuum chamber was filled with argon gas at atmospheric pressure where water vapour and molecular oxygen were controlled within limits of 0.0003 and 0.0002 %, respectively. The absorbed dose rate was 0.01 MGy/h. The film specimens was irradiated with doses 0.2MGy and the block samples B20, B40, B60, B80. B100 - with doses 0.2, 0.4, 0.6, 0.8, 1.0 MGy, respectively.

Tensile test was carried out at room temperature, and

the stress-strains (S-S) curves for the dumb-bell specimens were recorded with a cross head speed of 20 mm/min. The yield strength, tensile strength, elongation at break, and modulus were obtained from the SS curves.

A Perkin-Elmer LS-5 fluorescence spectrometer was employed for the emission and excitation spectra collection at ambient temperature. Absorption spectra were recorded using Lambda-9 spectrophotometer. The resolution of the sub-bands present in complex spectral profiles was achieved using the "Curvefit" utility of OPUS 5.0 software (Bruker Optic GmbH). A Gaussian shape was adopted for the components, and the fit was optimized with a local least squared method.

II. Results and discussion

Figure 1 shows the stress-strain (S-S) curves of PTFE (thickness 3 mm) after irradiation up to 20 MRad under vacuum at 330 °C. Both elongation at break and tensile strength do not decrease so much for these irradiation doses.

The big changes in the mechanical properties of PTFE are due to chain scission by irradiation, so the experimental results indicate that the probability of chain scission increases with irradiation under the temperature below the melting temperature. Above 350 °C. the chain scission is much accelerated, which may be accompanied by the thermal depolymerization of PTFE. At around 340 °C the radiation induced chemical reactions are changed very much, where the chain scission is much reduced or the other reactions, such as crosslinking, may proceed with the irradiation.

Dose dependence at 330 °C has been investigated. Yield strength, where the stress at the knee point of S-S curve at the strain about 5 % in Fig. 1, increases with dose. The modulus, which is determined from the slope of initial line in the S-S curve, increases with dose as well. The increase in both yield strength and modulus

indicates the formation of network structure in PTFE, that is, the crosslinks between the molecular chains.

Thus the changes of mechanical properties of PTFE irradiated at around 330 °C in the molten state are completely different from those of PTFE irradiated below the melting temperature. The changes and the behavior in the molten state strongly suggest the network formation by the radiation induced crosslinking in PTFE. Especially, increase in yield strength and in modulus indicates the increase of network density in PTFE molecules. Generally, it is accepted that these values increase with increasing crosslinking density for linear polymers. The crosslinking between PTFE polymer chains should prevent the crystallization of the molecules from the molten state.

Luminescence and coloring. Film samples.

Radiation modification of film specimens at a temperature of 330 °C and a dose of 0.2 MGy leads to visually observed changes. Some films acquire a color ranging from light gray (sample 1, 5) to light brown (samples 2, 3). Films 4 are colorless. When exposed to UV light at a wavelength of 365 nm, films 1–3 exhibit bright light yellow fluorescence, which is well detectable visually; films 4, 5 display very weak emission. The appearance of color and fluorescence properties for radiation-modified PTFE indicates the formation of polymer-chain segments containing a conjugated π -bond system.

The effect of colour and fluorescence appearance in modified films is apparently due to the traces of molecular oxygen dissolved in the bulk of polymer. The similar effect was observed when PTFE was treated by atomic oxygen [9]. The samples 1 - 3 outgassed at r.t. that originally contained dissolved in polymer oxygen demonstrate very intense fluorescence. The increase oxygen concentration at increase of air pressure up to 100 mm Hg (sample 4) result in it significant quenching and loss of colours. On the other hand the samples with low concentration of oxygen (samples 5 outgassed at high temperature) also show quite low fluorescence and

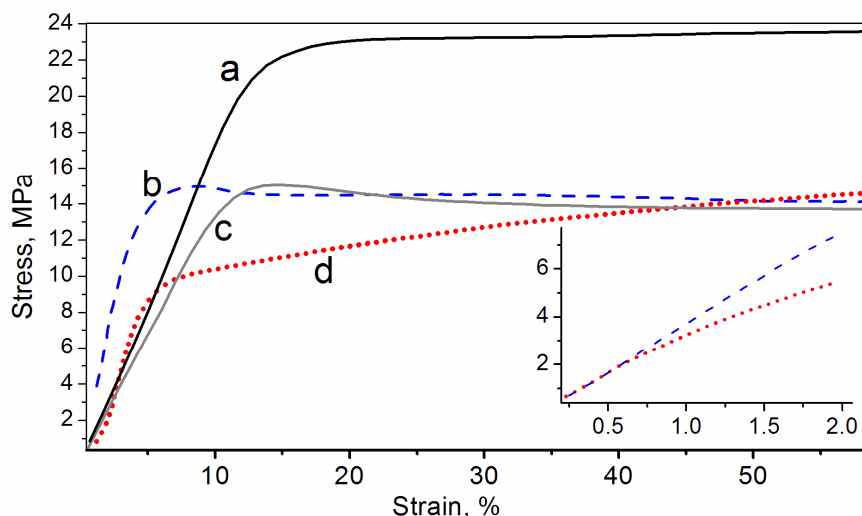


Fig. 1. Stress–strain curves for PTFE films: (d) an unirradiated sample, (a,c) samples subjected to electron-beam irradiation in vacuum at 340 °C and doses of 0.2 (c) and 1 (a) MGy [4] and (b)- γ - irradiation in vacuum at 330 °C and doses of 0.2 MGy (thickness 3 mm).

pale colors. Thus, presence of dissolved oxygen traces in polymer and irradiation under vacuum with residual pressure 10^{-3} - 1 mm Hg contributed to such radiation-chemical process where formation and accumulation of fluorescent fragments with π -conjugated bounds comes out.

The synchronous scan fluorescence spectrum (SSF) was recorded on the λ_{exc} scale. The spectra of Figure 2 correspond to the highly fluorescent Sample 3. It clear that up to four types of highly fluorescent optical centers (OC) can be formed. To three of them corresponds peaks at wavelengths 350, 400 and 470 nanometers, and the fourth appeared to be a shoulder at 520 nm. The absorbance range of such OC can be established analyzing excitation spectrum. The three local peaks at wavelengths 340 nm, 390 nm, and 460 nm in the excitation spectra apparently due to the presence of three types of OC to which in SSF correspond short-wave range. Moreover, OC with long-wave range absorbance that should correspond to the shoulder at 520 nm of SSF spectrum in its excitation spectrum can not be detected, by contrast the absorbance band position can be derived from SSF. Taking into account that the scanning spectrum was recorded with adjustment of 20 nm ($\Delta\lambda = \lambda_{exc} - \lambda_{fl}$) it is possible to assume that the maximum absorption of this center should be around 500 nm.

Fluorescence spectrum of the irradiated samples is a broad spectral curve with one or two wide maxima, position of which strongly depends on wavelength of excitation (fig. 2). It also confirms quite complex band, i.e. presence not only single OC but several of them.

Absorption spectra of films represent the curves which ordinates steadily decrease in intensity by wavelength increasing. Absences of obvious peaks on broad spectral curves indicate that number of the OC of absorption is much more in quantity than number of OC

producing fluorescence. Significant part of OC can behave introducing or less fluoresces, or its absence at all.

Block samples. Originally, before exposure to the irradiation, block PTFE samples at day light had a white color, and opposite dark at UV light i.e. do not produce visible fluorescence. After irradiation, the samples getting yellow color and exhibit fluorescent properties, as observed visually upon UV illumination. Surface color of polymers changes with radiation doses increase, starting from light gray (sample B 20) up to the brown one (sample B 100). The thickness of colored layer of the blocks does not exceed 1 mm. It has turned out that already on depth of an order 50 μ m coloring of all irradiated samples (independently on the dose) is similar. After removal of a layer 50 μ m thick all samples have light yellow color.

Fluorescence spectra of a sample surface, recorded at excitation wavelength $\lambda = 290$ nm, are shown on fig. 2. The most intensive fluorescence exhibit sample B20 that was irradiated with the least dose – 0.2 MGy. By increasing the radiation, dose the intensity of emission band decreases: for sample B40 – 1.8 times, at B60 – 3 times, at B100 – 10 times. The shape of a fluorescence spectrum profile changes as well. Its maximum significantly shifts to the higher wavelengths; approximately up to 470 nm for the sample B20 and to 600 nm for B100 sample.

The described dependence of fluorescence spectra of a sample surface with irradiation dose is due to the fact that the colored surface plays a role of the optical filter. Actually, it turned out, that samples with an outlying thin surface layer (at about 50 μ m) have not only similar coloring but also all, including sample B80, possess quite intense fluorescence with almost identical intensities and spectrum shapes.

As well as in case of films samples, fluorescence of

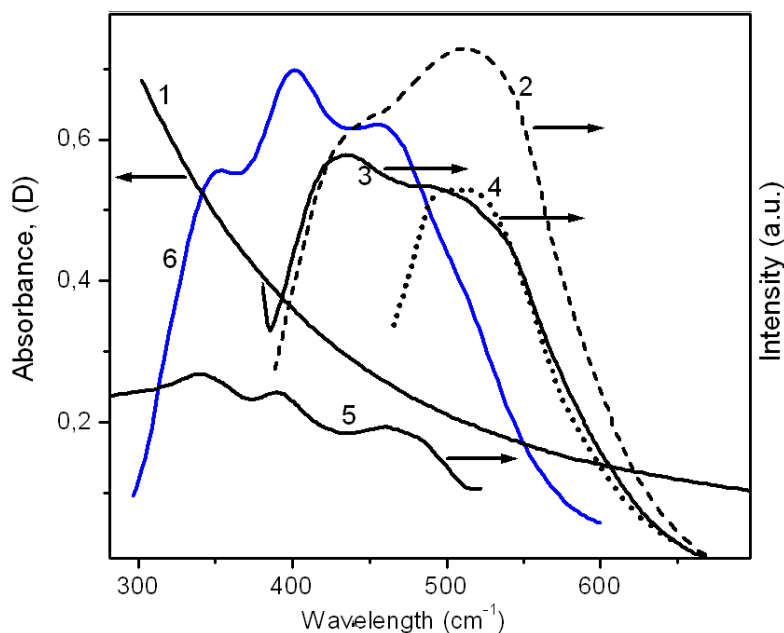


Fig. 2. Absorption spectra (1), fluorescence spectra at excitation wavelengths $\lambda = 365$ nm (2, 3) and $\lambda = 450$ nm (4), excitation spectrum at the fluorescence registration wavelength $\lambda = 535$ nm (5) and synchronous scanning fluorescence spectrum with $\Delta\lambda = 20$ (6) of the irradiated samples. Curve 2 – sample 2, the other spectral curves is of sample 3

the irradiated block samples also depends on wavelength of excitation that suggest the presence of the several emission centers in them. To establish emission range of OC formed in the irradiated samples the deconvolution of its spectral profile has been carried out using Gaussian function for each combination mode.

Using combination four Gaussian function good agreement with experimental spectrum profile and lowest error of discrepancy has been attained. Namely, four centers of emission and absorption was attributed to the subbands with their maxima at 370 nm (centre I), 414 nm (centre II), 470 nm (centre III) and 532 nm (centre IV) respectively. Therefore four OC with intense fluorescence are formed in irradiated film species and block samples and absorbance centers accordingly following 300, 345, 390 and 470 nm.

Thus on the basis of obtained experimental data it can be concluded that OC responsible for the surface coloring of irradiated blocks PTFE and fluorescence centers – are completely different centers having different nature and structure. It confirmed not only by their difference of the distribution in the bulk of the sample. The coloring centers absorb in all visible area of a spectrum (even most light colored samples have reflection power not exceeding 20 %) whereas the fluorescence centers producing visible luminescence, possess bands of absorption in the range of a near ultraviolet, by contrast the centers III, IV absorb partially in violet and dark blue range. In the presence of the centers with such absorption, the modified samples can get only light yellow or golden-yellow color.

In order to clarify the process of colored centers formation on a surface of the irradiated samples and to identify their structure, a further additional research is required. In this work, we introduced only main important points. Apparently, in their formation take part low-molecular fluorine-containing compounds liberating from heated up PTFE during process of a γ -irradiation. They interact with an uncontrollable impurity, which present in argon gas, and also with a products allocated on the chamber walls. Some of the formed compounds are colored. They are adsorbed on a surface of samples and give them certain color. At the same time the colored surface of samples plays a role of the optical filter, which decreases the intensity and leads to shifting of the fluorescence spectrum maximums.

Concerning the structure of fluorescence OC the situation is more clear. Recently [5 - 8] we have reported, that these centers have polyene structure (- CF=CF-) n,

where $n = 4 - 7$. This assumption was based on following facts. It is well known that the presence of conjugated double bonds in the polymers exposed to UV-light, ionizing radiation and/or thermal treatment is detectable by means of luminescence and UV-absorption spectroscopy. The main feature of these polymers is that their main molecular chain consists of carbon atoms as well as in case of PTFE. Such effect mentioned above was observed in polystyrene, polyvinyl alcohol, polyvinylchloride and some others polymers [10].

More precisely structure of OC I-IV was defined in ref. [4] by selection of the model polyen compounds with $n = 4 - 7$ using available literature data on fluorescent characteristics of various compounds. The absence in spectra of modified PTFE fluorescence bands similar to polyen with $n = 2$ and 3 is explained by that these structures don't fluoresce [11].

Thus, in the present work spectral characteristics of absorption and fluorescence of OC formed in the γ -irradiated PTFE are specified. It was established that the different OC are responsible for fluorescence and coloring of a surfaces of the modified PTFE. The fluorescence centers are formed both at the near-surface region as well as in the bulk of the sample. Their concentration slightly changes at the various dosage of gamma-radiation (which ranged from 0.2 to 0.8 MGy), while the concentration decreases noticeably with a deepening into sample. It was confirmed, that the molecular oxygen traces in a sample play an important role in formation of the optical emission centers.

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