EPR INVESTIGATIONS OF γ-IRRADIATED POLYTETRAFLUOROETHYLENE/CdS NANOCOMPOSITES

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It is shown that g-factor values for PTFE/CdS nanocomposites at dose 5kQr corresponds to free electrons. The nonlinear dependence of signal intensity on craze number is observed with increase of craze cycle in EPR spectra.

Keywords: γ – irradiation, nanocomposites, polytetrafluoroethylene, magnetic field, EPR-spectra, dielectric properties, dielectric loss, dielectric constant, crazing, g-factor.
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INTRODUCTION

Nowadays the significant number of works dedicated to modification of surface and structure of polytetrafluotoethylene (PTFE) are carried out. PTFE films are some of the best dielectrics, its dielectric properties weakly depend on field frequency at wide temperature intervals [1,2]. Moreover, the value of dielectric loss tangent of angle (tg δ) and dielectric constant (ε') significantly increase at influence by *γ*-irradiations and/or by accelerated electrons [3]. It is shown that the increase of tg *δ* at *γ*-irradiation is connected with formation of peroxide macro-radicals of tail and medial types as a result of destruction and oxidation processes [3,5].

The study of regularity of formation and stabilization of primary paramagnetic centers (free radicals, electrons) induced by electric and /or magnetic fields promotes to development of new approach at study of primary processes in *γ* -irradiated nanocomposites. With the aim of their oriented modification, EPR method is the unique one for the study of the change of radical g-factor, local fields, their surrounding (note that *g* -factor is the ratio of mechanical moment to magnetic one which is equal to 2,0023) and for the evaluation the spin density, their anisotropy and structural changes in polymers [14 - 16].

The technological questions of modification of PTFE are the one of important ones for improvement of polymer exploitation characteristics. Moreover, the radiation technology plays the important role. The radiation resistance (in 100 – 200 times) and the physic-mechanical properties of PTFE are improved [17 – 19]. In work [20] it is shown that at electron irradiation the films from matched PTFE with thermostability 450 -500^{0}C are obtained with beam density by 10^2-10^3 μA/cm^2.

The investigation of influence of γ-irradiations and uniaxial orientation of crystallized polymers, in particular, PTFE, polyethylene terephthalate (PETF) and etc. are important for development of new "track" membranes with pores on the surface with diameter by 20-500nm order. The formation of nano compositions on the base of craze PTFE, PETF and luminescent fillers CdS, ZnS is the one of actual tasks at obtaining of flexible luminescent compositions. It is important to note that detail study of polymer craze processes allows us to vary the porosity and significantly increase the quantity of introduced additives in the polymer.

EXPERIMENTAL PART

The oriented nanocomposites PTFE/CdSZnS are obtained by "craze" method, i.e. by the way of uniaxial orientation of PTFE films in the adsorption-active medium from 30% isopropanol solution in water [7,13]. The binary mixture CdS/ZnS at ratio 90:10 vol.% (the value of forbidden band width E_g=2,42eV for CdS, and E_g=4,27 eV for ZnS [12]) is used with the aim of extension of luminescence composition sensitive region. Note that the crazing is the polymer modification universal method, their structure and properties at introduction of low-molecular additives in polymers, in particular, in cases where additives aren't compatible with polymers.

EPR investigations are carried out on spectrometer EMX Plus (Bruker). The magnetic field intensity 600mmT and modulation frequency 10^5Hz, interval of amplitude modulation interval is 0÷2mT.

The samples are put into glass tube with diameter 3mm and measurements are carried out at T=300K. The resonance frequency is 9,75 GHz.

g-factor is defined from equation $E=h\nu=g\mu_B \cdot B_0$.

$g=\frac{h\nu}{\mu_B \cdot B0}$, where μ_B is Bore magnetron, is the natural value of electron magnetic moment.

The technique of uniaxial polymer orientation in adsorption-active medium and the technique of dielectric parameters (tg δ, ε, ρ_v) are described in [21].

The introduction of fillers in oriented PTFE in the stage of polymer color change is carried out in four cycles.

The sample is carefully washed in distillate water after each cycle of nanoparticle formation in polymer pores [22].

The nanocomposite samples are irradiated by γ-quantums ^{60}Co in source MPX- γ-20M. The dosimetry is carried out by ferrosulfate method.

The study of peculiarities of radical- formation role at *γ*-irradiation of nanocomposites polytetrafluoroethylene/CdS is the aim of the given work.

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EXPERIMENTAL RESULTS AND THEIR DISCUSSION

The irradiation of solid state, in particular polymer composites, should be accompanied but not only by its ionization and by formation of new electron traps-radicals, and by release of already captured electrons from the traps. Note that the blanching process and role of O_2 molecules dissolute in polymers in radical-formation takes the important place [23]. Besides, the influence of constant magnetic field on electron transitions between Zeeman levels [4,14] are the essential tasks in radiation physical chemistry of nanostructured materials.

EPR spectra of PTFE samples/after 3 cycles of CdS introduction under condition ΔH=7,64G and g=2,0028 are shown in fig. 1. *g*-factor values allow us to propose that it connects with electron centers in matrix. From the given spectrum it is seen that at H=3480-3500G the narrow singlet the appearance of which can be connected with free electrons in composite. At the increase of *γ*-irradiation dose up to 5kQr the EPR spectrum narrowing is observed and values of g-factor achieves the maximum, further it decreases with increasing irradiation dose.

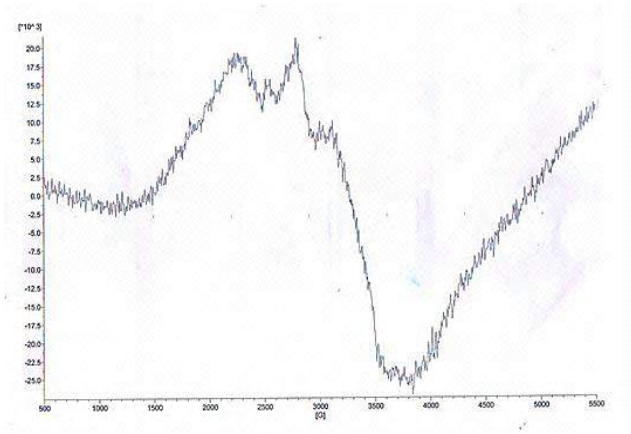

Fig.1. EPR spectrum of PETF/CdS nanocomposite samples crystallized at 3 treatment cycles and *γ*-irradiated up to 3 kQr doses.

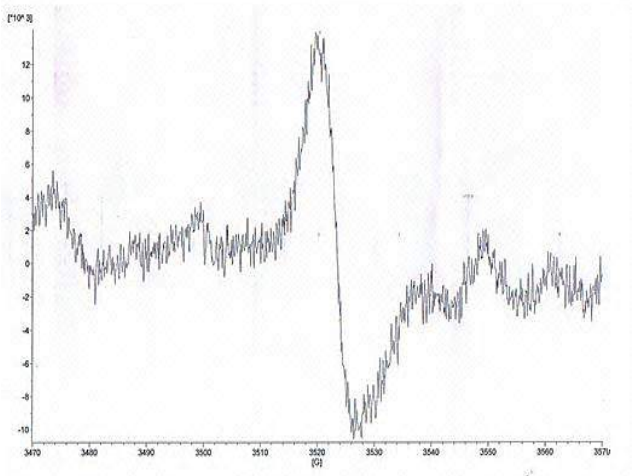

Fig.2. EPR spectrum of PETF/CdS nanocomposite samples crystallized at 3 treatment cycles and *γ*-irradiated up to 5 kQr doses.

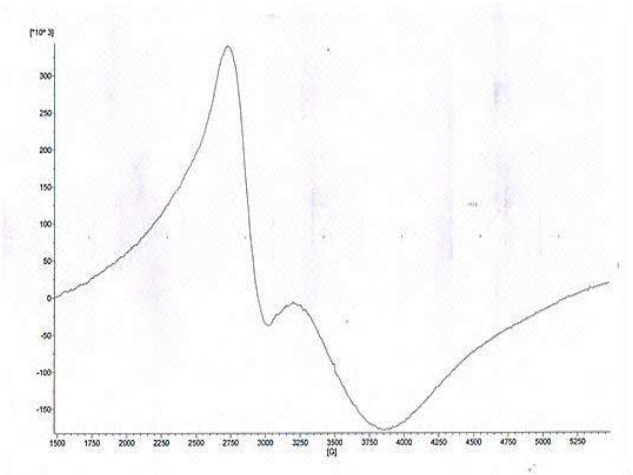

Fig.3. EPR spectrum of PETF/CdS nanocomposite samples *γ*-irradiated up to 5 kQr doses after 3 cycles of CdS implantation.

Table

Oriented samples	Initial ones			After γ-irradiation, 3kQr			After γ-irradiation, 5kQr		
	ΔH, G	g	I,rel. un.	ΔH, G	g	I, rel. un.	ΔH, G	g	I, rel.un.
PTFE	1110	2,160	45,75	103,8	2,149	40,5	-	-	-
PTFE/CdS 3 cycles	1192	2,060	41,25	971,5	2,168	290	669,2	2,0203	169
PTFE/CdS 16 cycles	-	-	-	987,8	2,16	135	958	2,244	129

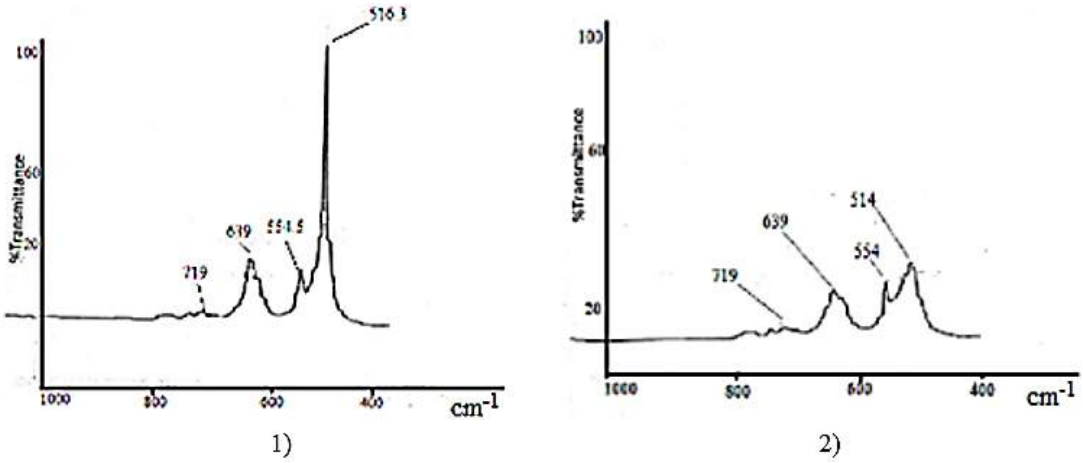

Fig.4. IR-absorption spectra in region 400 – 1000cm^{-1} of PTFE/CdS samples after 6th cycle of nano-CdS implantation.

The another important peculiarity of EPR spectra of PTFE/CdS nanocomposites is that the significant change is observed at increase of craze cycle in EPR spectra, narrow band signal disappears, the wide band signal appears after *γ*-irradiation (fig. 2 and fig. 3). EPR spectrum of PTFE/CdS composite samples irradiated up to doses 5kQr after 3 cycles of CdS implantation is shown in fig. 3.

It is revealed that values of *g*-factor firstly increase, passes through maximum at dose 5kQr and further decrease tendency is observed in the dependence on irradiation dose of PTFE/CdS samples with increasing *γ*-irradiation time. The changes of g-factor values and intensities of EPR signals in the dependence on implantation cycle of CdS nanoparticles and irradiation dose are given in the table.

From the table it is followed that the values of g-factor decrease after *γ*-irradiation by 3-5kQr dose. The ratio of wurtzite and sphalerite components of CdS which are reflected in the changes of g-factor values in the dependence on quantity of "craze" nanoparticles of CdS in PTFE matrix.

IR-spectra of the samples in the dependence on craze cycles are obtained for the study of structural changes in PTFE and nanocomposites on the base of oriented PTFE/CdS in the dependence on adsorbed nanoparticles in polymer. IR-spectra of absorption for the oriented samples PTFE (curve 1) and samples after CdS implantation craze (curve 2) are shown in fig. 4.

From the comparative analysis of these spectra it is seen that the absorption intensity at 516cm^{-1} decreases with increasing cycle number of nano-CdS implantation in oriented PTFE samples and CdS quantity. After three cycles the given peak intensity decreases in 4,5 times. Besides, 639cm^{-1} and 516cm^{-1} peaks widen with increasing implanted CdS nanoparticle number.

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