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EFFECT OF γ -RADIATION ON THE CHARGE STATE OF PTFE / CdS NANOCOMPOSITES

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Abstract: The impact of γ -irradiation up to ~ 10 kGy dose was studied on the charge state of the PTFE / CdS nanocomposites generated on the basis of AAM oriented in nanoporous films of polytetrafluoroethylene with the subsequent formation of nanoparticles in these pores by layered chemisorption method. It was shown that, the change of the charge state at γ -irradiation related redistribution of concentration of radiation defects and quasi-stable radicals in the polymer matrix and interphase boundary of polymer-filler of PTFE / CdS composite. The change of ratio of crosslinking process and destruction depending on the irradiation dose changes the mobility of molecular segments of polymer matrix and the concentration of active centers. And this leads to a change in the charge state and active electret properties of PTFE / CdS nanocomposite.

Keywords: PTFE, CdS, nanocomposite, γ -irradiation, charge state, polarization of corona discharge, thermal depolarization, crosslinking, destruction, electret.

1. Introduction

Polymer composites of different composition, containing as modifiers of nanocomponents are perspective materials. In such composites, there is observed a unique combination of electrical, magnetic, thermal, mechanical and other properties which cannot be achieved in conventional polymeric composites. Realization of such properties of composites is conditioned by high activity of nanofillers due to their high surface and structural activity, ability to be center of crystallization of polymers and easy adaptation to the conditions of the external exposure to environmental conditions [1-3].

Currently, obtaining of polymer-inorganic hybrid materials with nanometer level of dispersion components, having complex specific physical properties is an actual problem. The synthesis of particles of a new phase in porous polymer matrix, obtained by the mechanism of crazing in the adsorption-active liquid media (AAM), consisting of a system of fibrils and pores of nanometric level of dispersion, can be as an original approach for the problem [3-5].

Polymers, as the base materials for generating electrets, in many cases, do not require necessary mechanical, thermophysical and other properties, required for their practical application. At the same time, life demands materials with new properties. Therefore, it is advisable to use a composition consisting of a polymeric binder and fillers of different nature for obtaining electret materials with desired properties. There occur new structural elements that can be a trap of charge carriers that cause a change of electret dielectric characteristics during filling of polymers with dispersed fillers in composite materials [6-9].

Oriented polymer films are one of the most promising materials for making stable electrets with high electret difference of potential U_k [10]. At the orientation drawing in the surface layers of polymer films, there occurs the process, which is accompanied by generating of new nanostructured formations. These structures can be energetically deep center of trapping charge in polymers. The stability of electret state in non-polar polymer films is mainly determined by localized states of trapping center, ie the concentration of energetically active traps on the surface and in the volume [10,11].

From the literature, it is known that, it is possible to modify the properties of polymers and composites on their basis of ionization radiation. Today, modification of the characteristics of materials of γ -radiation is actual and is the basis of radiation materials science [12-14]. Due to this, the aim of the present work is to study the effects of γ -radiation on the charge state of the PTFE/CdS nanocomposites based on oriented in AAM nanoporous films of polytetrafluoroethylene with subsequent formation of nanoparticles in these pores by chemisorption. The effects of γ -radiation were affected in two different modes:

- In the first case, PTFE / CdS nanocomposites are formed based on pre-irradiated with different doses of PTFE.
- In the second case, γ - irradiation exposed to formed PTFE / CdS nanocomposites.

2. Experimental

We have previously investigated the electret properties and charge state of PTFE / CdS nanocomposites formed on the basis of uniaxially oriented PTFE films in AAM by the method of layered chemisorption [15]. In the present study it was investigated the effect of γ -irradiation on the electret properties of PTFE / CdS nanocomposites formed on the basis of oriented PTFE films and pre- γ -irradiated (Co^{60} at $T=290\text{C}$) PTFE films.

Porous nanostructure was generated on surface layers of the initial and pre- γ -irradiated PTFE films by the orientation drawing method in AAM with subsequent formation of CdS nanoparticles in these pores by the method of layered chemisorption.

The orientation of spade PTFE films was carried out under constant stress, after 10 days of irradiation for stabilization of the structure. CdS nanoparticles in oriented polymer PTFE matrix with 20 microns thicknesses were formed using CdCl and Na₂S solution with certain concentration (CdCl-0.05mol / l; Na₂S-0,1mol / l) by the method of ion-layered chemisorption. Samples with three, six and nine cycles of formation of CdS nanoparticles were obtained and each cycle was lasting 30 minutes. Samples of PTFE / CdS composites were washed in distilled water and finally dried in a desiccator after each cycle.

Today, the method of Corona discharge is most common in the production of polymer electrets. The advantages of corona electrification are simplicity of equipment, relatively high speed of the process and uniform distribution of charge on the surface. Proceeding from this, the polarization of obtained samples was carried out by effect of corona discharge in the needle-plane at the stress on the needle $U_{kor} = -7\text{kV}$, for $t = 3\text{minutes}$. The choice of negative corona is conditioned by two factors:

- Firstly, a negative corona is considerably less sensitive to the presence of water vapor, than the ions generated at the positive corona. Consequently, in the intensity the development of charge accumulation of positive corona contributes a significant contribution and the relative humidity of the air. [8]
- Secondly, the samples, charged by a negative corona at discharge give considerably high current than positive corona in their charging [9].

The distance between the electrodes was about $\sim 1\text{cm}$. Assessment of the charge states of polarized samples was carried out by comparing Thermally Stimulated Depolarization (TSD) current spectra. TSD current spectra was taken after 15 minutes of polarization in the temperature range of $293\text{-}473\text{C}$ using electrometric amplifier U5-11 in linear increase of temperature of the sample with the rate of $\sim 5\text{ C / min}$. Irradiation of samples is carried out on the installation of MPX- γ -25M based on isotope Co^{60} .

3. Results and discussion

The study of charge state of the samples of corona electret from PTFE and PTFE/ CdS composites shows that TSD current spectra has maximums with different polarity (inversion), and the temperature position (Fig. 1).

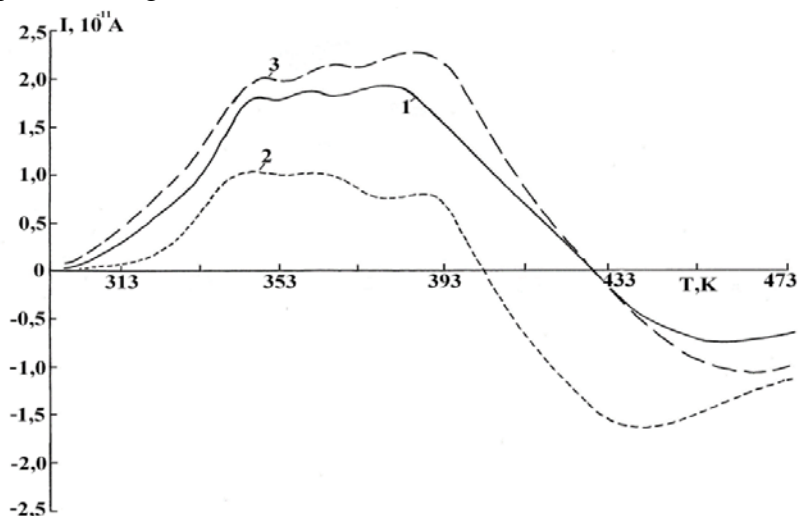


Fig.1 TSD current spectra of oriented PTFE films and PTFE / CdS composite with different numbers of cycles of formation: 1 - the original; 2 - 3 cycles; 3 - 6 cycles;

Comparison of TSD current spectra of oriented PTFE films and PTFE / CdS composites stored for six months shows that the intensity of the low temperature peak decreases (3 cycles), with increasing number of cycles of formation, but this maximum increases in amplitude and area with a further increase (6 cycles). A maximum is observed in high temperature parts of TSD current spectrum of oriented films and composites with six cycles of formation at the temperature of ~ 453 C. But, a composite with three cycles of formation of observed TSD maximum has relatively high amplitude and covers a large area equivalent to more charge in the temperature of ~ 453 C. As the table shows, high-value of ratio of area of high-temperature maximum to the low temperature in the TSD current spectra have samples of PTFE / CdS composite formed during three cycles.

Table 1 Ratio of area of high-temperature maximum to low-temperature in TSD current spectra for PTFE and PTFE/ CdS composites

Area	PTFE	PTFE/3cycle.CdS,	PTFE/6cycle.CdS,
S ₁ , rel. units	10.15	4.13	12.2
S ₂ , rel. units	1.68	6.26	2.42
S ₂ /S ₁	0.17	1.52	0.2

A further increase of cycles of formation is accompanied by coating surface of the film of nanoparticles and increasing of concentration of charge with low-temperature relaxation. We believe that, the formation of CdS nanoparticles in PTFE crazes, decreasing the mobility of macromolecules contributes to the effective accumulation and stabilization of electret charges in them. At six cycle, held charges accumulated on the surface nanoparticles of screening penetration of them into the composite lead to an increase of surface charge density and thus a

relatively low-temperature maximum. Polarization of charges, corresponding to high-temperature maximum of TSD current spectra, is formed under the influence of the local field created by surface charges.

We consider the first for the study of effects of γ -radiation on the charge state of PTFE / CdS nanocomposites from two different offered regimes, i.e., in this case the PTFE/ CdS nanocomposites are formed based on PTFE films pre-irradiated with different doses. In this case, crazy formation and porous structure are formed on the basis of irradiated PTFE films and subsequently generated nanoparticles interact with macromolecules of pre-irradiated PTFE, there is no direct exposure to gamma radiation on the formed nanoparticles. It is known that PTFE is relatively radiation - sensitive among the polymers, predominates destruction processes even at low doses of radiation, and there are various kinds of radicals and free charges in the volume of polymer. The radical formation increases with increasing radiation dose passing through a maximum at doses of $2 \div 5\text{kGr}$ and thereafter falls [16,17]. Radical formation continues in polymeric materials, even after cessation of exposure. Irradiated PTFE film hardly undergo mechanical orientation, but this small orientation ($\sim 20\text{-}30\%$) allows you to form PTFE / CdS nanocomposites on their basis by the method of layered chemisorption. Fig. 2 shows the TSD current spectrum of composites, formed on the basis of PTFE films irradiated with pre-dose $1,7\text{kGr}$, with a different number of cycles of formation. It can be seen that maximums in TSD current spectra are detected at $\sim 383\text{C}$, and the values of accumulated charge in samples extremely vary with the increase of cycles of formation. The maximum of accumulated charge is detected for samples with six cycles of formation.

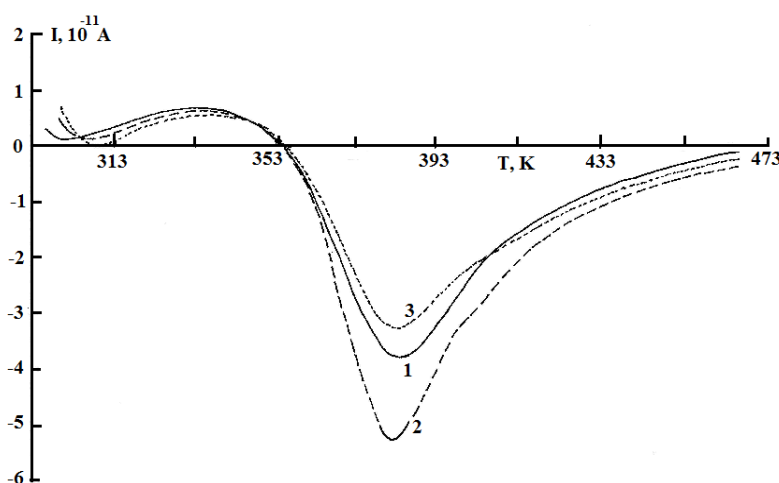


Fig.2 PTFE / CdS composite is formed on the basis of pre-irradiated PTFE film up to $D = 1.7\text{kGr}$ (2 hours) dose: 1- 3 cycles CdS; 2- 6 cycles of CdS; 3- 9 cycles CdS;

As it has been shown by the authors [16,17], macroradicals which have certain activity are formed at PTFE after irradiation. We believe that, active radicals and formed nanoparticles interacting with each other, form a layer of the polymer composition on the surface and in a certain depth of the polymer matrix. Interphase boundary and the accumulated charge increase with the increase of a number of cycles of formation of the particles, respectively. But, as it is seen from the spectra, there observed a decline of accumulated charge in samples with nine cycle of formation of nanoparticles that happens as a result of full cover of the surface of the polymer film of cadmium sulfide nanoparticles.

It is known from the comparison of TSD current spectra of PTFE/CdS composites formed in three cycles depending on the dose of pre-irradiation that, the increase of dose leads to mixture of the maximum of TSD current in the direction of low temperature (Fig. 3). The same pattern is also preserved for composites with six cycles of formation. Polymer films, irradiated at low

doses, are relatively better subjected to mechanical orientation, and relatively highly porous structure is formed in them. As a result, the formation of the nanoparticles occurs in a relatively deep area of the polymer film. The increase of doses of PTFE irradiation leads to decrease of mechanical properties of polymer matrix and decrease of the size of crazes, respectively. And the decrease of the size of crazes leads to formation of nanoparticles on the surface of polymer, which causes the change of location of the maximum of TSD current to lower temperatures.

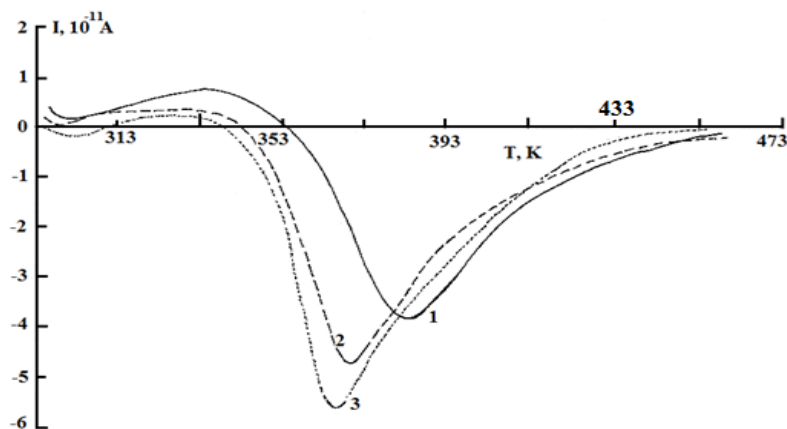


Fig.3 TSD current spectra of samples of PTFE / 3cycle CdS composites formed on the basis of pre-irradiated PTFE at different doses: 1- $D = 1,7\text{kGr}$; 2 - $D = 4,2\text{kGr}$; 3 - $D = 8,4\text{kGr}$;

We consider the second for the study of effects of γ -radiation on the charge state of PTFE / CdS nanocomposites from offered regimes, where γ - irradiation is exposed to formed PTFE / CdS nanocomposites. In this case, γ - radiation interacts with the nanocomposite, ie gamma radiation simultaneously affects both the matrix, and filler as formed nanoparticles.

Fig. 4 shows TSD current spectra of irradiated and non-irradiated samples of PTFE / 3cycle-CdS nanocomposites. It is clear from spectra that, a relatively high accumulation of charge is observed in samples, irradiated up to 1,7kGr dose.

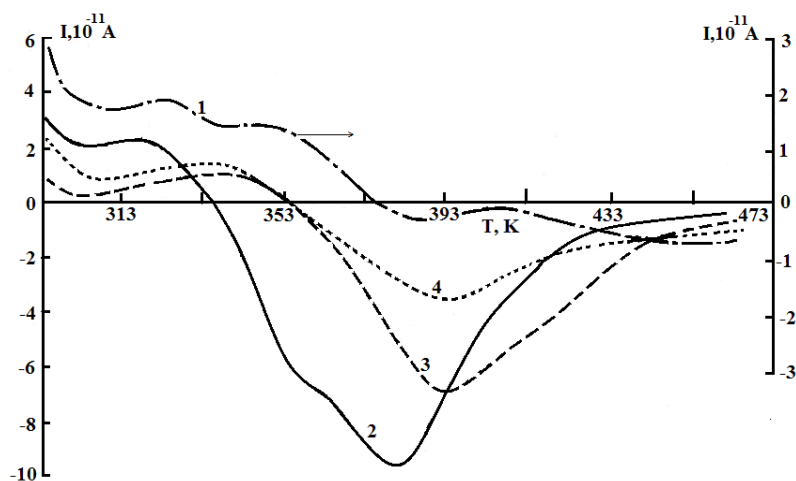


Fig.4 Spectra of current of TSD samples of PTFE / CdS composites formed at three cycles and modified γ - irradiation at different dose levels after the formation; 1 - initial PTFE / CdS; 2 - $D = 1,7\text{kGr}$; 3 - $D = 4,2\text{kGr}$; 4 - $D = 8,4\text{kGr}$.

This tendency is also preserved for PTFE / CdS composites with other filler content. Radicals and free charges are formed after gamma irradiation of samples of PTFE / CdS

nanocomposites in their volume and surface layers. After the cessation of irradiation of macroradicals formed by certain depth of the polymer nanocomposite should lead to a change in its charge state and modification their electroactive properties. The above assumption is confirmed by comparing TSD.

As it was shown in [16, 17], the dependence of the concentration of formed radicals at PTFE has an extreme character with maximum in the area of absorbed dose $2 \div 5$ kGr after irradiation. Comparison of our results with the results of the authors [16], allows to say that the concentration and the value of radiation defects in PTFE / CdS samples, irradiated at low doses, are relatively high, and their concentration decreases with increase of radiation dose. As a result, the relatively high value of accumulated charge is observed for the samples at low values of the radiation dose. It's clear that, with the increase of radiation dose of maximum TSD current decreases in amplitude and shifts to higher temperatures. So the increase of radiation dose is accompanied by the increase of the destruction in vulnerable sections of the polymer in the craze, i.e. in fibrils. Appeared elements of destruction of polymer chain entering as deep traps formed by interaction with the surface of CdS nanoparticles, which leads to confusion of maximum (kr.3). But as experiment shows, the concentration of vulnerable sections of low and further increase of radiation dose leads to decrease of maximum amplitude (kr.4) in a result of increase of degradation of matrix.

On the other hand, it is known that under the influence of ionizing radiation at the polycrystalline particles of nano-sized CdS there occurs agglomeration processes as a result of recrystallization of the amorphous phase in the crystal and the growth of particle size [18]. But, increase of particle size is accompanied by a decrease of effective surface and leads to a decrease of concentration of accumulated charge, respectively. At the same time, in temperature 453-473C, flat and broad maximum is observed, which is connected with space charges trapped in deep traps with a broad energy spectra in a volume of PTFE polymer.

Figure 5 shows TSD current spectra of PTFE / CdS composites with different filler content, modified γ -irradiation up to a dose of 1.7kGr.

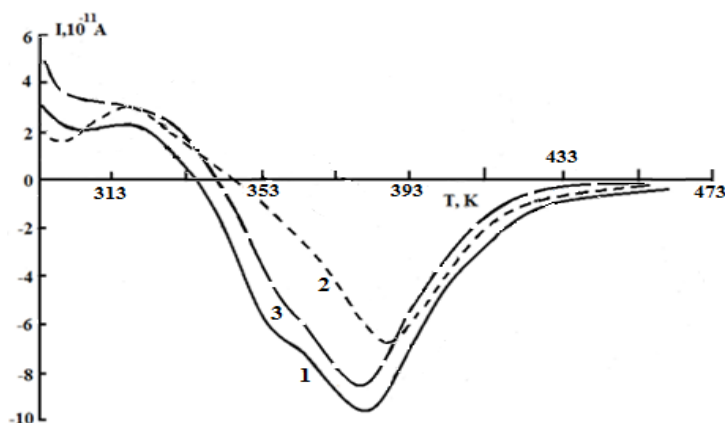


Fig. 5 TSD current spectra of PTFE / CdS composites of modified γ -irradiation up to a dose of 1.7kGr (2 hours): 1- 3 cycles; 2- 6 cycles; 3- 9 cycles of formation

It is seen that with increasing filler content at first the maximum is shifted to higher temperatures with subsequent return to the low-temperature area in nine cycles. For composites with three cycles of formation due to low content of nanoparticles, the maximum is formed by the interaction of free radicals with the free charges and minor charges released from the interface boundary. We believe that the filler content increases with the increase of formation of cycles from three to six, there occurs an increase of the effective surface of the interface boundary of polymer-filler and correspondingly improves the interaction of the polymer matrix

with nanoparticles, ie free radicals and maximum charges interact with nanoparticles. It, in its turn, leads the charge accumulation in relatively deep traps in the interface, and high-temperature maximum in TSD current spectra.

But further increase of cycles of formation up to nine cycles followed by coating the entire surface of CdS nanoparticles, while the prevalence of stored charge in the low-energy capture centers in the surface of the nanoparticles and thus mixing the high to low temperatures. Besides it, an increase in the space charge can effect on mechanical destruction of the polymer matrix in the result of impact of gamma radiation and the charge accumulation in these mechanical defects. In conclusion we can say that, the redistribution of the concentration of radiation defects and quasi-stable radicals in PTFE / CdS composite at γ -irradiation is an important reason to change their charge state and active electret properties.

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ВЛИЯНИЕ γ -РАДИАЦИИ НА ЗАРЯДОВОЕ СОСТОЯНИЕ НАНОКОМПОЗИТОВ ПТФЭ/CdS

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Резюме: Исследованы воздействия γ -излучения до дозы ~ 10 кГр на зарядовое состояние нанокomпозитов ПТФЭ/CdS созданных на основе ориентированных в ААС нанопористых пленок политетрафторэтилена с последующим сформированием наночастиц в этих порах методом послойной хемосорбции. Показано, что изменение зарядового состояния при γ -облучении связано перераспределением концентрации радиационных дефектов и квазистабильных радикалов в полимерной матрице и межфазной границе полимер-наполнитель композита ПТФЭ/CdS. Изменения соотношения процесса сшивки и деструкции в зависимости от дозы облучения изменяет подвижность молекулярных сегментов полимерной матрицы и концентрации активных центров. А это приводит к изменению зарядового состояния и активных электретных свойств нанокomпозита ПТФЭ/CdS.

Ключевые слова: ПТФЭ, CdS, нанокomпозит, γ -облучение, зарядовое состояние, поляризация коронным разрядом, термодеполяризация, сшивка, деструкция, электрет.

γ -ŞÜALANMANIN PTFE/CdS NANOKOMPOZİTLƏRİNİN YÜK HALINA TƏSİRİ

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Xülasə: Politetraftoretlenin (PTFE) adsorbsion aktiv mühitdə oriyentasiyası zamanı yaranan nanoməsəmələrdə kimyəvi sorbsiya üsulu ilə nanohissəciklərin formalaşdırılması ilə alınmış PTFE/CdS nanokompozitin yük halına ~ 10 kQy qədər dozada γ -şüalanmanın təsiri tədqiq olunmuşdur. Göstərilmişdir ki, γ -şüalanmanın təsirindən kompozitin yük halında baş verən dəyişikliyin səbəbi polimer matrisada və polimer-doldurucu fazalararası sərhəddində radiasion defekt və kvazistabil radikalların konsentrasiyasının dəyişməsidir. Şüalanma dozasından asılı olaraq tikilmə və destruksiya prosesləri arasında münasibətin dəyişməsi polimer matrisada molekulyar seqmentlərin yüyürlüklüyünün (mütəhərriqliyinin) və aktiv mərkəzlərin konsentrasiyasının dəyişməsinə səbəb olur. Bu iş PTFE/CdS nanokompozitinin yük halının və aktiv elektret xassəsinin dəyişməsi ilə nəticələnir.

Açar sözlər: PTFE, CdS, nanokompozit, γ -şüalanma, yük halı, tacşəkilli boşalma ilə polyarizasiya, termodepolyarizasiya, tikilmə, destruksiya, elektret.