

ELECTROPHYSICAL PROPERTIES OF GAMMA-IRRADIATED POLYETHYLENE TEREPHTHALATE (PETPh/CdS) NANO-COMPOSITS ON THE BASE OF POROUS MEMBRANES

M.A. NURIYEV, A.A. SHUKUROVA, A.SH. MAMMADOVA, A.I. GASIMOVA

Institute of Radiational Problems of Azerbaijan NAS

Az 1143, B. Vakhazade, 9, Baku, Azerbaijan

The electrophysical properties of initial and irradiated *PETH/CdS* nano-composites obtained on the base of industrial track membranes from *PETPh* with three and twenty of formation cycles are investigated in the present work. It is shown that the observable effects in frequency dependence of electrophysical properties of *PETH/CdS* composites are connected with polarization change in matrix interphase boundary with filler and CdS nano-particles in *PETPh* near-surface region and radiation processes in polymer matrix at influence of gamma radiation. The study of frequency dependence of resistivity of porous *PETPh* and composites on *PETH/CdS* base shows that the resistivity of porous *PETPh* decreases as a result of destruction after influence of gamma radiation and the taking place matching leads to the increase of physical interaction in boundary nano-particle – polymer, and resistivity of *PETH/CdS* composites relatively increases.

Keywords: Polyethylene terephthalate (*PETPh*), porous track membrane, dielectric constant, dielectric losses, resistivity, interphase boundary, layerwise chemisorption, irradiation dose.

PACS: 61.80Ed;72.80. Tm;72.80. Le

INTRODUCTION

Last time the fields of technique and science which are connected with formation of nano-dimensional materials and structures on their base rapidly develop. The big interest to this direction is connected with unique properties which substance particles have in nano-dimensional scale. It is known that material nano-dimensional particles have unique optical, electrophysical and magnetic properties in comparison with unitary materials of the same chemical composition [1,2].

In this connection with this fact, the scientific investigations are directed to development of synthesis methods of nano-dimensional semiconductor crystals and compositions on their base for the problem solving in instrument engineering, biology, ecology and medicine [3–5]. The metal chalcogenides of CdS, CuS, ZnS types are the most studied from these semiconductor materials. They are obtained in the form of powders, films, solutions and are introduced in the composition of the different polymer matrixes [6–11].

The saving of the nano-particle stability and their optical characteristics connected with them are the important fact in synthesis process. For this problem solving the nano-particles are introduced in the different polymer matrixes and thus their fixation in attitude positions is carried out [12–14]. That's why the investigations of nano-particle synthesis methods and their stabilization by different manners are the actual problems.

The nano-particle synthesis method in tracks of polymer membranes obtained at their irradiation by heavy particles is the one of the perspectives nano-composite obtaining method. We consider that tracks of these membranes are well for stabilization of nano-particle different types including chalcogenide particles [15–16]. The formation of these materials requires the carrying out of the fundamental investigations of the processes carrying out at their formation and influence of different external factors on their electrophysical

properties. The porous structure of polyethylene of low density (*PELD*) and polyethylene terephthalate (*PTPh*) have been obtained earlier by us by the method of orientation extract [17]. *PELD/CdS* and *PTPh /CdS* nano-composites are formed on the base of obtained porous structures by the method of layerwise chemisorption and their electrophysical properties before and after gamma irradiation are studied [18–19]. The results of electrophysical characteristic study in particular, frequency-temperature dependences of the main dielectric parameters (ϵ , $\text{tg}\delta$ and ρ) of *PETPh/CdS* nano-composites obtained on the base of industrial track membranes from *PETPh* with three and twenty formation cycles modified by gamma irradiation, are shown in the given work. The study of these composite properties is of big interest for their application in the different fields of science and electrotechnique.

EXPERIMENTAL PART

PETPh/CdS nano-composites obtained on the base of industrial track membranes (porous films) from *PETPh* by thickness $h \sim 27 \mu\text{m}$ prepared in *JNR* (Dubna) are the objects of investigation. The pore concentration in these membranes is $n = 5 \cdot 10^9 \text{ cm}^{-2}$. CdS nano-particles are formed in pores of track membranes of *PETPh* by the method of layerwise chemisorption [20]. The samples of porous *PETPh* and nano-composites *PETPh/CdS* on its base with three and twenty cycles of CdS formation are investigated. The supposed schematic image of *PETPh/CdS* nano-composite cross-section with three and twenty cycles of CdS formation is shown in fig.1. We suppose that the formed CdS nano-particles in porous polymer matrix mainly form in near-surface layer of porous *PETPh* at layerwise chemisorption and the small part from these particles penetrates into matrix pores. The change of dielectric parameters (ϵ , $\text{tg}\delta$ and ρ) in alternative field is measured with the help of emittance *E7-20* at rate $2,5 \text{ K/min}$. The sample irradiation is carried out on installation *MPX- γ -25M* on the base of Co^{60} isotope.

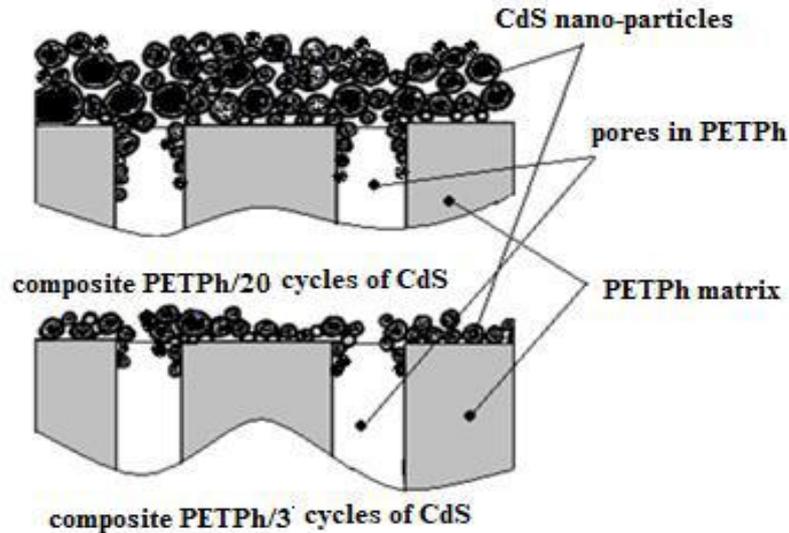


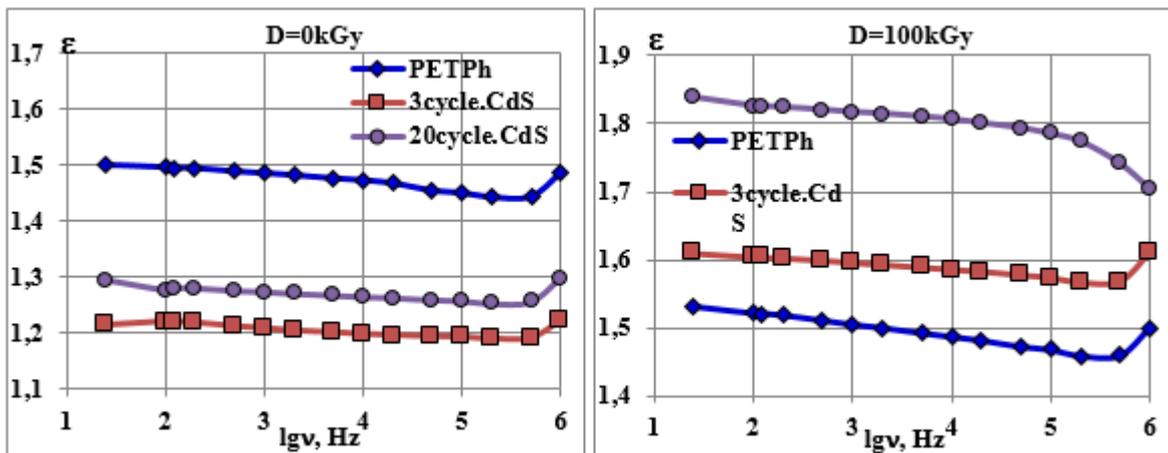
Fig. 1. Schematic image of cross-section of *PETPh/CdS* nano-composites with three and twenty cycles of CdS nano-particle formation.

RESULT DISCUSSION

The frequency dependences $\varepsilon(\nu)$, $tg\delta(\nu)$ and $lgr(\nu)$ of polyethylene terephthalate (*PETPh*) and *PETPh/CdS* composites on its base with different cycles of formation which are irradiated at doses 100, 300 and 500Gy are shown in presented figures below.

The frequency dependences of dielectric constant of initial and irradiated porous *PETPh* and *PETPh/CdS* composites on its base with different formation cycles are shown in fig.2. It is known that values of *PETPh* dielectric constant is in interval $\sim 3,1 \div 3,25$ [21,22]. But tracks lead to the formation of porous structure on the surface and in *PETPh* volume as a result of the fact ε values decrease and as experimental data show that these values are in region $\sim 1,6$ for polymer and in region $\sim (1,2 \div 1,3)$ for nano-composite. We consider that this fact causes to increase of CdS nano-particle concentration increase, high value of dielectric constant of CdS ($\varepsilon \sim 9$) and changes of the thickness of each layer. As it is seen from the frequency dependences the

influence of gamma irradiation leads to ε value increase up to $\sim 2,6$ for *PETPh* and up to $\sim 1,8$ for nano-composites on their base. We consider that such change of ε values is the result of transversal matching taking place after irradiation influence in polymer matrix and improvement of polymer matrix interaction with CdS nano-particles in polymer near-surface layer. The given results (fig.1) show that sample dielectric constant decreases with increase of measuring field frequency. Such change shows the relaxation character of dielectric constant dependence for matrix and all composites. The relatively high value of dielectric constant at low frequencies with filler increase is caused by increase of effective surface of interphase layer and charged accumulated in it taking part in relaxation process Maxwell-Vagner in composite material. The tendency to the increase of ε dielectric constant value is observed in the end of measured frequency range ($\nu > 5 \times 10^5 \text{ Hz}$).



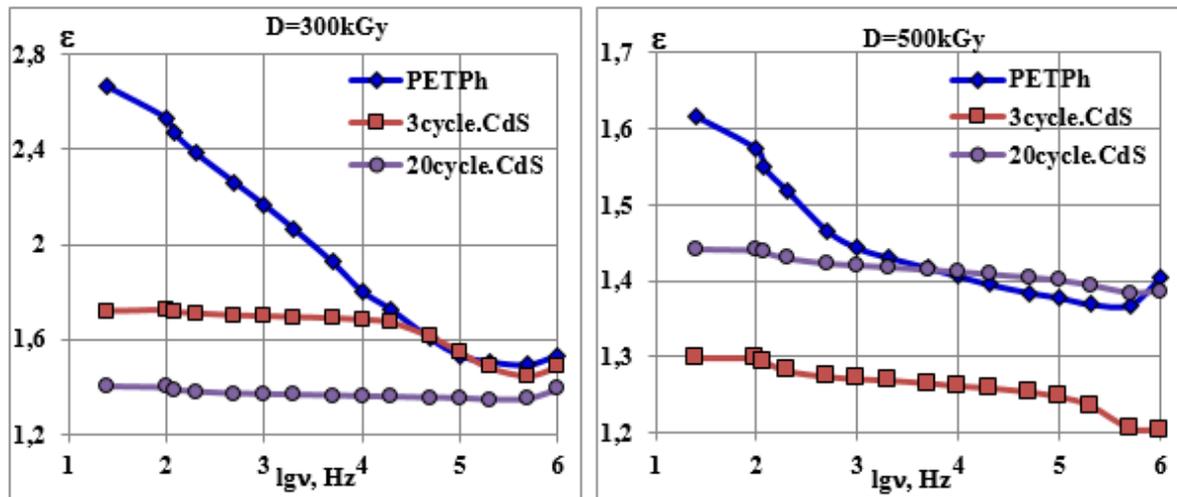


Fig.2. The frequency dependences of dielectric constant of initial and irradiated porous PETPh and PETPh/CdS composites on its base with different number of formation cycles.

As it is seen from the frequency dependences after influence of gamma irradiation the dielectric constant of *PETPh* increases up to doze 300Gy with the further decrease at 500Gy. It is considered that such trend of a curve causes to maximum matching at irradiation up to doze 300Gy. This leads to the increase of polymer crystallinity and increase of effective surface of

interphase between crystalline and amorphous regions of *PETPh*. Besides ϵ increase can cause the polarity of polyethylene terephthalate itself. This proves the maximums in relatively low-frequency region of $tg\delta=f(\nu)$ dependence of porous polyethylene terephthalate (fig.3).

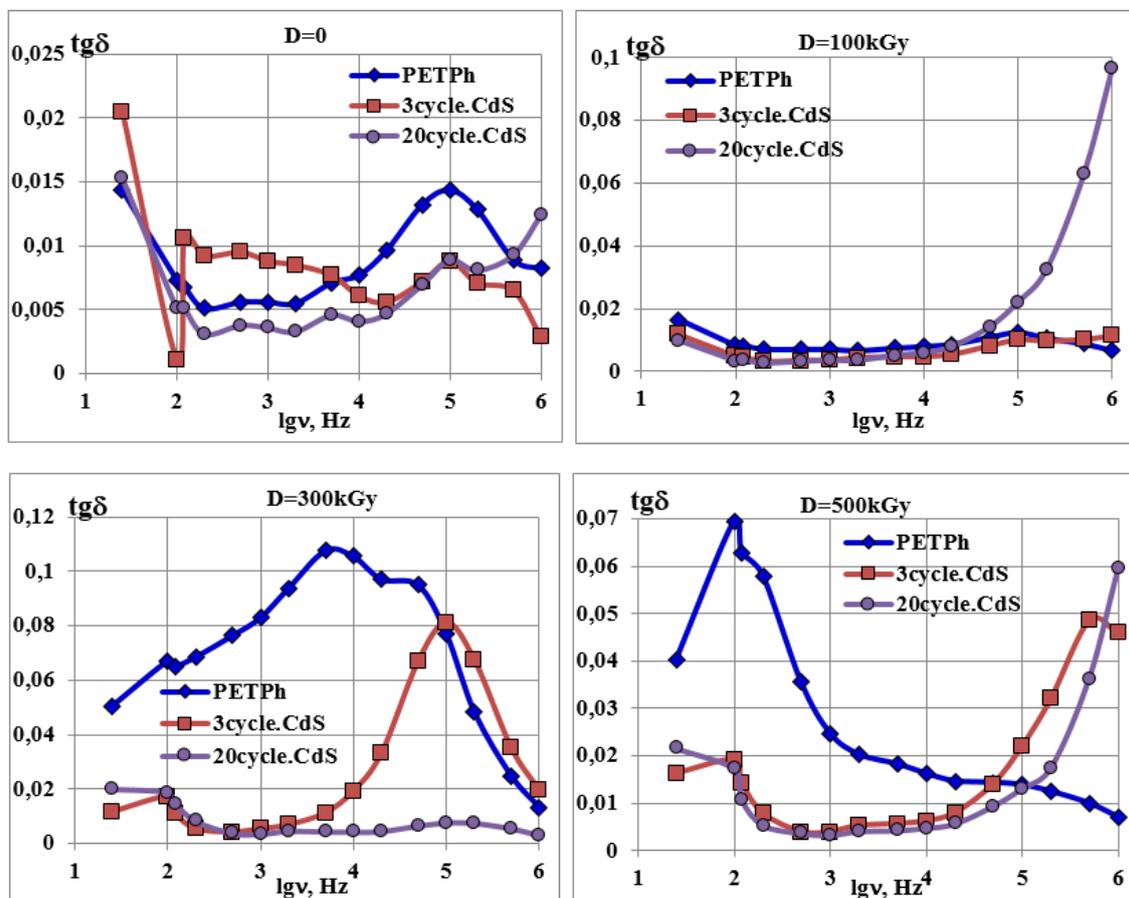


Fig.3. The frequency dependences of dielectric losses of initial and irradiated porous *PETPh* and *PETPh/CdS* composites on its base with different number of formation cycles.

The increase of dielectric constant is observed in frequency dependence of *PETPh/CdS* composites obtained at 3 and 20 cycles of formation and irradiated up to dose 100kGy. It is considered that ϵ increase is connected with both the increase of nanoparticle interaction between each other and active products on polymer surface appearing after initial destruction in polymer matrix chains, polarity and piezoelectricity of CdS particles [23]. The above mentioned proves the increase of *PETPh/CdS* composite dielectric constant in initial stages of irradiation dose (up to 100kGy) with the increase of filler content and observable increase of $\text{tg}\delta$ of composites *PETPh/20* cycles of CdS irradiated by dose 100kGy at high frequencies (fig.3). The observable increase of $\text{tg}\delta$ of *PETPh/20* cycles of CdS irradiated at dose 100kGy is connected with both increase of active product interaction formed after irradiation (for example, low-molecular impurities and polar groups C-O) by each other and CdS nano-particle polarity.

The further increase of irradiation dose (up to 300kGy) leads to decrease of ϵ value for both composites. The composites with high filler content (of *PETPh/20*th cycles of CdS) has relatively low values of dielectric constant and dielectric loss tangent (fig.2 and fig.3) than the composite with low content (*PETPh/3* cycles of CdS). It is considered that observable fact is connected with increase of transversal matching process between polymer chains and interaction improving in interphase boundary polymer-filler which leads to decrease of relaxor mobility in polymer composite *PETPh/CdS*. The further increase of radiation dose (up to 500kHz) leads to stabilization of ϵ value as a result of destruction dominating in polymer composites *PETPh/CdS* and relaxor polarization increase in CdS. The above mentioned proves the maximums in the dependence of $\text{tg}\delta=f(\nu)$ composites in frequency region $5 \cdot 10^6 \text{Hz}$ and which corresponds to filler dipole polarization. Besides, in this case the big

role of volume charges in composite polymer layer formed at irradiation by dose 500kGy which leads to their interlayer division at polarization.

The frequency dependences of resistivity of initial and irradiated *PETPh* and *PETPh/CdS* composites on its base with different number of formation cycle are presented in following figure (fig.4).

It is known that frequency dependence of resistivity of non-homogeneous structures is described by following regularity:

$$\rho = \rho_0 \nu^s \tag{1}$$

where s is constant which characterizes the change of resistivity in the dependence of frequency. S parameter value defines the charge carrier mobility character, i.e. material electric conduction mechanisms under influence of alternating electric field. If the condition $s < 1$ is carried out then carrier motion is the translation one, if $s > 1$ then it is considered that carrier motion is the localized one, i.e. the displacement or oscillation of the charge takes place between localized states [24, 25]. If for the value of this constant the condition $0,7 \leq s \leq 1$ is carried out, then it is considered that hopping of electric conduction is the right one for the measured material [26]. It is considered that composite electric conduction *PETPh/CdS* on the base of porous *PETPh* which has the heterogeneous structure also can be described by expression (1). Taking logarithm of this expression we obtain the following formula for the calculation of s parameter value:

$$s = \Delta(\lg\rho) / \Delta(\lg\nu) \tag{2}$$

The values of parameter s calculated from dependences $\lg\rho=f(\nu)$ (fig.4) for the initial and irradiated porous *PETPh* and *PETPh/CdS* composite is presented in the table.

Table

s parameter values calculated from dependences $\lg\rho=f(\nu)$

№	D, kGy	CdS contene in the composites	$\Delta(\lg\nu)$	$\Delta(\lg\rho)$	s
1	0	0; 3ts.; 20ts.	2,0	2,26	1,13
2	100	0; 3ts.; 20ts.	2,0	2,48	1,24
3	300	0	2,0	1,84	0,92
		3ts.	2,0	3,2	1,6
		20ts.	2,0	2,4	1,2
4	500	0	2,0	1,72	0,86
		3ts.; 10ts.	2,0	2,62	1,3

As it is seen from the table the condition $s > 1$ is mainly carried out for the s parameter value for irradiated and initial samples, the irradiated samples of porous *PETPh* at doses 300 and 500kGy for the which the condition $0,7 \leq s \leq 1$ are the exclusion. As it is above mentioned, the carried-out condition $0,7 \leq s \leq 1$ corresponds to electric conduction hopping, i.e., in irradiated samples at doses 300 and 500kGy of porous *PETPh* the charge motion takes place in the volume or

on pores of the surface. At condition $S > 1$ it is considered that carrier motion is the localized one, i.e., the charge displacements (oscillations) between localized states is observed. In first case the sample resistivity relatively decreases and becomes closer to semiconductors and in second place the sample resistivity relatively increases and becomes close to dielectrics where interlayer and dipole polarization processes dominate.

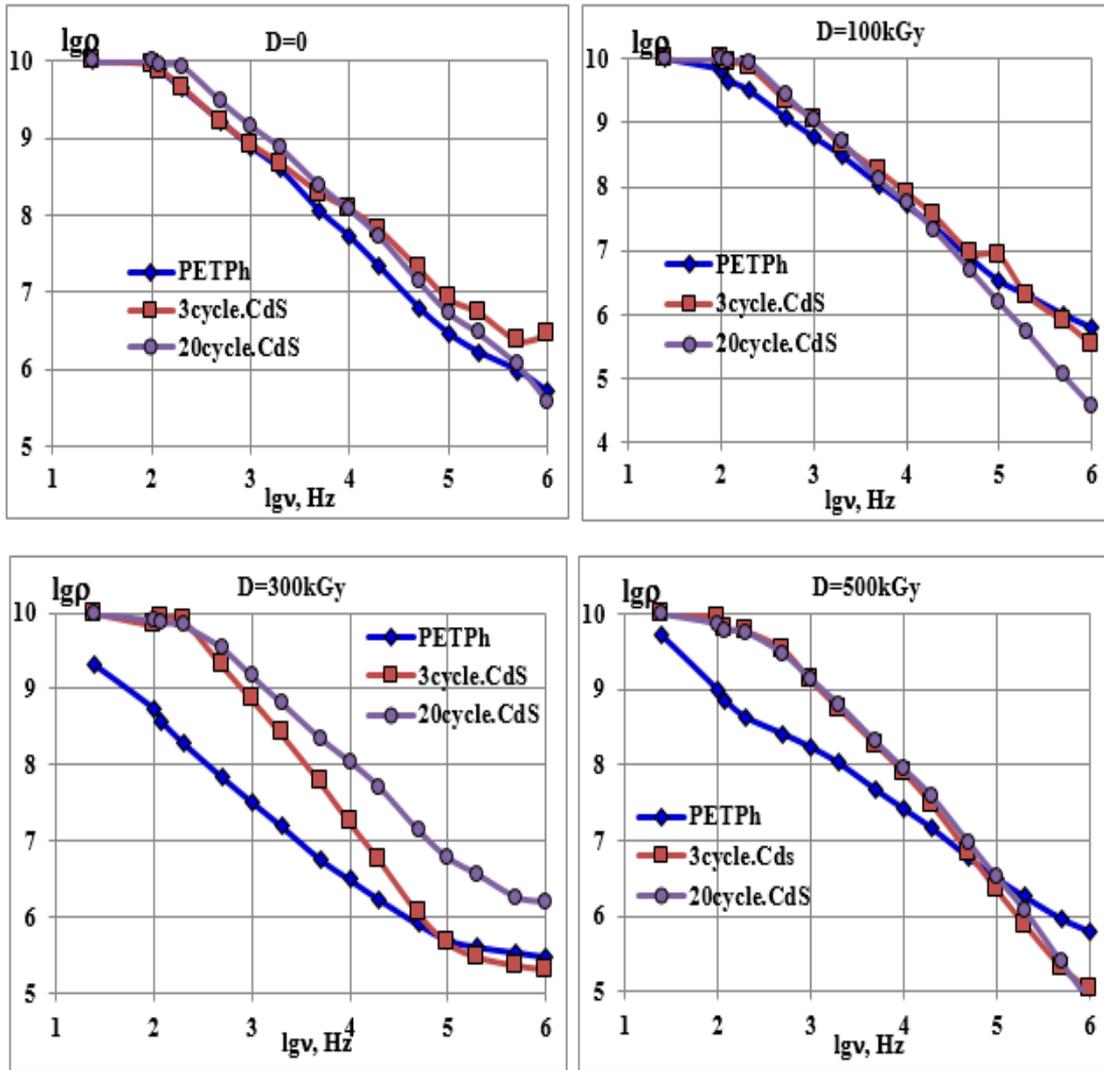


Fig.4. The frequency dependence of resistivity of initial and irradiated porous *PETPh* and *PETPh/CdS* composites on its base with different number of formation cycles.

The temperature dependences of resistivity of initial and irradiated porous *PETPh* and *PETPh/CdS* composites on its base prove the above-mentioned version of conduction mechanism (fig.5). The observable minimums in low-temperature region in temperature dependence of resistivity of polymer and composites are considered as the result of retained moisture desorption. From the dependences it is seen that samples of irradiated *PETPh* have the relatively low value of resistivity which coincides with obtained data from frequency dependences for the irradiated samples at doses 300 and 500kGy.

By other hand, the relatively low inclination of direct composites irradiated by doses 100 and 300kGy in comparison with *PETPh* inclinations in dependence high-temperature part can be estimated as dominating of matching in this dose region for the composites. The thickness increase with the increase of cycle number in near surface layer from CdS nano-particles leads to the decrease or disappearance of minimum depth in low-temperature region as the result of increase of physical

interaction between nano-particles and polymers after influence of gamma radiation.

CONCLUSION

Thus, the observable effects in frequency dependence of *PETPh/CdS* composite dielectric properties obtained on the base of porous track membranes of *PETPh* are connected with both the change of polarization in matrix interphase boundary with filler and CdS nano-particles in near-surface region of *PETPh* and radiation processes of polymer matrix at influence of gamma radiation. By study of irradiation of resistivity frequency dependence of porous *PETPh* and composites on its base of *PETPh/CdS* it is established that resistivity of porous *PETPh* relatively decreases after influence of gamma radiation as the result of taking place destruction. And after interaction of gamma radiation the taking place matching leads to the increase of physical interaction in boundary nano-particle –polymer and composite resistivity of *PETPh* relatively increases.

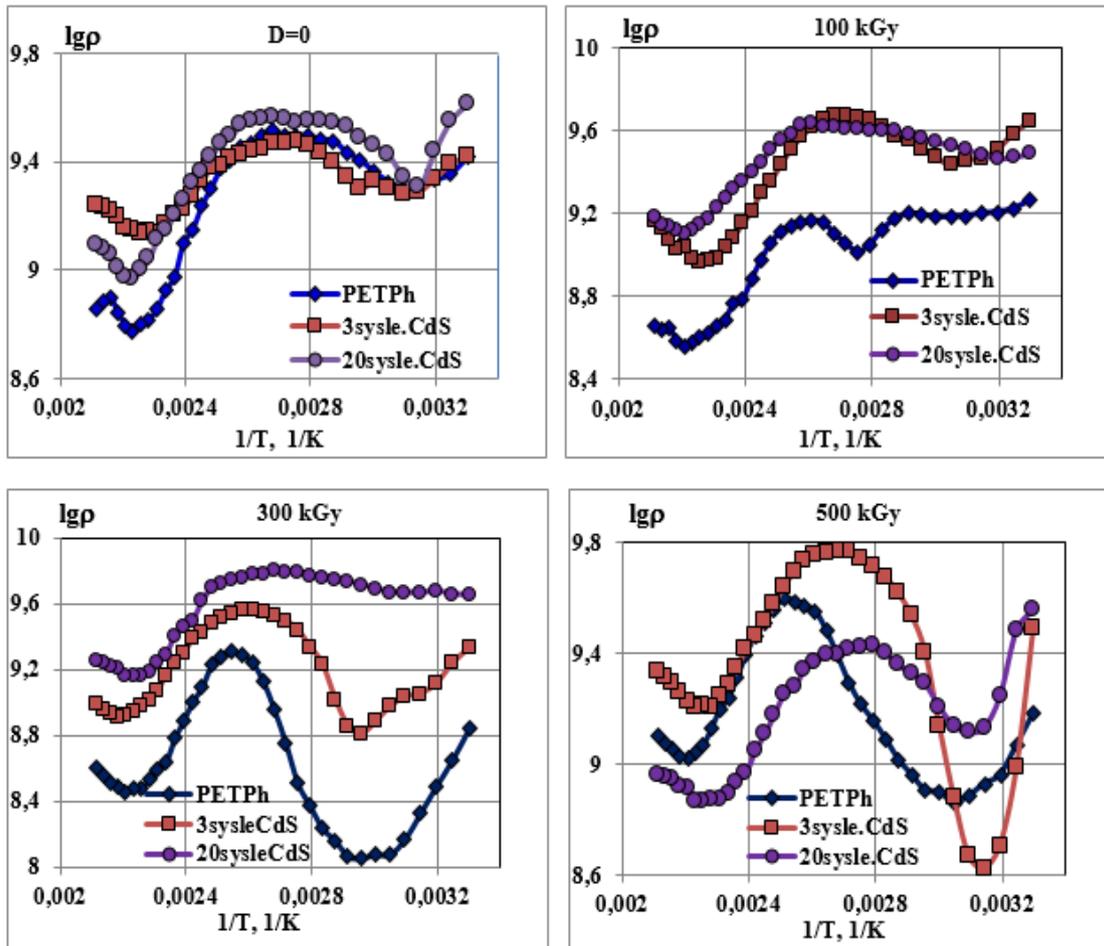


Fig.5. Temperature dependence of resistivity of initial and irradiated porous PETPh and PETPh/CdS composites on its base with different number of formation cycles.

- [1] J. Goldberger, He R., Y. Zhang. Single-crystal gallium nitride nanotubes., Nature, 2003, vol. 422, pp. 599-602.
- [2] J.C. Hulteen, C.R. Martin. A general template-based method for the preparation of nanomaterials., Journal of Materials Chemistry, 1997, vol.7, pp.1075-1087.
- [3] R.F. Khairutdinov. Chemistry of semiconductor nano-particles., Chemistry successes, 1998, vol. 67, № 2, pp. 125-139.
- [4] A.A. Rempel. The nano-technologies, properties and application of nano-structured materials., Chemistry successes, 2007, vol. 76, № 5, pp. 474-500.
- [5] B.P. Chandra, V.K. Chandra, P. Jha. Luminescence of II-VI Semiconductor Nanoparticles., Solid State Phenomena, 2015, vol. 222, pp.1-65.
- [6] D. Denzler, M. Olschewski, K. Sattler. Luminescence studies of localized gap states in colloidal ZnS nanocrystals., J. Appl. Phys., 1998, vol. 84, N 5, pp. 2841-2845.
- [7] R. Lozada-Morales, O. Zelaya-Angel, G. Torres-Delgado. Photoluminescence in cubic and hexagonal CdS films., Appl. Surface Sci. 2001. vol. 175–176. pp. 562-566.
- [8] M. Hayne, B. Bansal. High-field magnetophotoluminescence of semiconductor nanostructures, Luminescence. 2012. vol. 27. №3. pp. 179-196.
- [9] X. Sun, L. Xie, T. Wang, et. al. Optical fiber amplifiers based on PbS/CdS QDs modified by polymers., Optics Express, 2013. vol. 21. №7. pp. 8214-8219.
- [10] B. Li, X. Zhang, L. Li et. al. (2014). White luminescence from CdS nanocrystals under the blue light excitation. Journal of Solid State Chemistry, 2014. vol. 214. pp. 108–111.
- [11] E.V. Ushakova, T.K. Kormilina, M.A. Burkova et. al. The Influence of Ligand Type on Self-Organization and Optical Properties of Cadmium Selenide Quantum Dots, Optics and Spectroscopy, 2017, vol. 122, №1, pp. 25–29.
- [12] I.A. Akimov, I.Yu. Denisuk, A.M. Meshkov. Nano-crystals of semiconductors in polymer matrix are new optical mediums., Optics and

- spectroscopy, 1992., vol. 72, № 4, pp. 1026-1032.
- [13] *N.M. Ushakov, K.V. Zapsis, G.Yu. Yurkov et. al.* Optical Properties of Cadmium Sulfide Nanoparticles on the Surface of Polytetrafluoroethylene Nanogranules., *Optics and Spectroscopy*, 2006, vol. 100, № 3, pp. 414–418.
- [14] *M.A. Zvaigzne, I.L. Martynov, V.A. Krivenkov et. al.* The Influence of the Quantum Dot/Polymethylmethacrylate Composite Preparation Method on the Stability of Its Optical Properties under Laser Radiation., *Optics and Spectroscopy*, 2017, vol. 122, №1, pp. 69–73.
- [15] *A.A. Mashenzeva, B.N. Aubakirov, M.B. Zdorovetz, A.B. Rusakova, A.T. Akilbekov.* Some aspects of argenthum precipitation in channels of track membranes on PETPh base, *Eurasia National University Buletin University named after L.N. Gumilyev*, 2012, №2, pp.84-92.
- [16] *E.Yu. Kanyukov, E.E. Shumskaya, M.D. Kutuzov D.B. Borgekov, I.E. Kenjina, A.L.Kozlovskii, M.V. Zdorovetz.* Ferromagnetic nano-tubes in pores of track membranes for the elements of flexible electronics., *Devices and measurement techniques*, 2017, vol. 8, №3, pp. 214–221.
- [17] *A.M. Magerramov, M.A. Nuriyev, A.A. Shukurova.* Electret properties of nano-structured films of Teflon., *Plastic masses*, 2012, №10, pp.7-9.
- [18] *A.M. Magerramov, M.A. Nuriyev, A.A. Shukurova.* On orientation of polyethylene irradiated films of low density and electric conduction of its compositions with nano-Cu₂S, *Perspective materials*, 2015, №5, pp.62-68.
- [19] *M.A. Nuriev, A.M. Magerramov, A.A. Shukyurova.* Electrical Conductivity of Nanocomposites Based on Low-Density Polyethylene and Cu₂S Nanoparticles., *Surface Engineering and Applied Electrochemistry*, 2018, vol. 54, №1, pp. 32–37.
- [20] *A.A. Shukurova, M.A. Nuriyev, A.I. Gasimova, I.M. Nuruyev, A.Sh. Mammadova.* The nanocomposites on the base of crystal polymers and cadmium sulfide., *Transactions, ANAS, series of phys-tech and math sciences, physics and astronomic*, №5, 2021, pp.121-127.
- [21] <http://www.newchemistry.ru/material.php?id=40>
- [22] *S.S. Federova.* The modification of electro-physical properties of polyethylene terephthalate films by ion-plasma precipitation of nano-dimensional coverings on carbon base., *PhD thesis, Moscow*, 2005, p.153.
- [23] *A.N. Georgibiani, M.K. Sheynkman.* Physics of the A₂B₆ compounds., *M.: Science*, 1986, pp.42–44.
- [24] *S.A. Sadikhov, D.K. Palchayev, J.Kh. Murliyeva, M.N. Alikhanov, M.Kh. Rabadanov, S.Kh. Gadjimagomedov, S.N. Kallayev.* Ac-electric conduction of BiFeO₃ ceramics obtained by the method of spark plasma baking of nano-powder., *Solid-state Physics*, 2017, vol. 59, № 9, pp.1747-1753.
- [25] *Yu.M. Poplavko, L.P. Pereverzeva, I.P. Raevski.* Physics of active dielectrics, *Rostov-na Donu.*, 2009, pp162-164.
- [26] *Shalini Kumari, N. Ortega, A. Kumar, S.P. Pavunny, J. W. Hubbard, C. Rinaldi, G. Srinivasan, J. F. Scott, and Ram S. Katiyar.* Dielectric anomalies due to grain boundary conduction in chemically substituted BiFeO₃, *Journal of Applied Physics*, 117, 114102, (2015), pp.1-13.

Received: 05.04.2022