

ELECTRET PROPERTIES OF γ -IRRADIATED COMPOSITES OF ULTRAHIGH MOLECULAR WEIGHT POLYETHYLENE/ α -SiO₂

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The influence of silicon dioxide (α -SiO₂) and the absorbed dose of γ -irradiation on the electret properties of UHMWPE+ α -SiO₂ composites were studied. It is established that the dependence of the stabilized charge on the volume content of the α -SiO₂ filler has an extreme character: at 1% α -SiO₂, the charge reaches a maximum and then decreases. TSD spectra show that the thermal stability of electrets of the UHMWPE+1 vol.% α -SiO₂ composite is improved. The nature of the TSD current of the films which preliminarily γ -irradiated up to 50...100 kGy doses proves that after γ -irradiation the charges injected from corona discharge zone are mainly accumulated in the subsurface layers. However, the deterioration of the electret properties of composites irradiated at high doses of γ -irradiation is related both to an increase in electrical conductivity so, and an increase in the rate of charge relaxation.

INTRODUCTION

It is known [1–3], that polymer composite materials with micro- and nanosized fillers are widely used in electrical engineering, electronics, condenser and cable technology. In addition, PCM has been successfully used as an emergency shield for a nuclear reactor, in the power supply system for artificial satellites and spacecraft, in sensors for monitoring the operation of radiological systems of nuclear reactors, where various types of ionizing radiation are always present that affect the operational properties of these materials.

Consequently, the success of these areas in providing new “functional” materials is to a certain extent related to the creation of stable electrets based on PCM. In this regard, in recent decades the interest of researchers to create new promising PCM and technologies has increased [4, 5].

One of the promising polymers meeting these requirements is ultrahigh molecular weight polyethylene (UHMWPE), since it possesses a unique complex of physic-chemical (high wear resistance, stability in corrosive media, high impact strength, low brittleness temperature, etc.) properties [3].

This allows you to create on its basis new composite materials for various applications. It is no accident that numerous studies [5–8] have been devoted to the study of the synthesis and physical properties of composites based on various polymers and inorganic fillers. In these works, the authors note that nanoscale silicon dioxide or aerosol (α -SiO₂) is one of the promising materials for creating radiation-protective composite structures [2, 6–10].

As already noted, polymers, and composites based on them, are exposed to various types of ionizing radiation during operation. However, despite the existence of experimental works [7, 8, 11–13], the question of the effect of radiation exposure on the electrophysical properties of polymer materials remains relevant, since composites based on them are widely used.

In this paper, we investigate the influence of γ -irradiation on the electret properties of UHMWPE+ α -SiO₂ compositions and reveal the character of the TSD spectra. It is known that electrets should be distinguished by high values and stability of the parameters (σ , τ). Therefore, nowadays in the scientific literature, there is an active search for disperse fillers, modifiers, additives capable of increasing the electret properties of polymers. The introduction of α -SiO₂ as a nanofiller is accompanied by an increase in the density and degree of crystallinity of UHMWPE in the composition of the composite, which in turn leads to a decrease in the conductivity, and thus can improve the stability of the electret state of the composite films based on them [14–19].

The purpose of this work is to obtain and study the electret properties of UHMWPE+ α -SiO₂, which can serve as the basis for the production of composite materials capable of operating under the γ -irradiation conditions.

EXPERIMENTAL PART

UHMWPE powder with an average molecular weight of $1.55 \cdot 10^6$, 65% degree of crystallinity and 190 °C melting point was used as a polymer matrix. The density and plastic transition temperature of the powder is 940 kg/m³ and 138...142 °C, respectively. Amorphous silica α -SiO₂ particles (Sky Spring Nanomaterials, Inc. Houston, USA) with a spherical shape and the size of 20 nm were used as the filler. A specific surface area of the filler particles is 160 m²/g. The density of the filler particles is 2.65 g/cm³ [3, 7]. The ratio of inorganic α -SiO₂ to UHMWPE was (1:99, 3:97, 5:95).

When manufacturing film samples, the following technological scheme was provide:

- mixing in the porcelain mortar of UHMWPE and α -SiO₂ powders;
- pressing a homogeneous mixture of component powders in a hydraulic press with heated plates at the

pressure of 15 MPa with holding at the temperature of 190 °C for 5 min and obtaining samples of composites in the form of disks with a diameter of 20 mm and a thickness of 80...50 μm;

– to ensure a reliable electrical contact between the sample and grounded electrodes made of stainless steel pressed on the surface of samples of an electrode of thin aluminum foil 7 μm thick, followed by cooling in a water-ice mixture (quenching regime).

All the concentrations indicated in the work are volume concentrations. The manufacturing mode of the composite allows obtaining the samples with recurring electro physical parameters. Polarization of samples from the side of a non-metallized surface was carried out in a corona discharge field with a polarization voltage of 6 kV in the needle-plane system with a needle distance 1 cm from the surface of the sample (charging time 300 s).

Immediately after polarization, to measure the thermally stimulated depolarization currents (TSD) of the samples, they were placed in a special screened and grounded heated measuring cell of the “sandwich” type with stainless steel pressure electrodes. The alignment of the electrodes was provided with a special mandrel. The electrodes were connected to an electrometric amplifier Y5-11, to the output of which a two-coordinate recorder “Endim 620.02” was connected, on which the current change was recorded as a function of temperature. The recording of the currents of the TSD in the temperature range of 20...190 °C was carried out with a linear increase in temperature at the rate of 2.5 deg/min.

The temperature of the sample was monitored with a copper-constantan thermocouple. Electrification of the samples was carried out by exposing them to corona discharge and ⁶⁰Co gamma-quanta. Measurement of the surface potential of electrets U_e was carried out periodically with the aid of the IPEP-1 device. The irradiation was carried out at the MRX-γ-25M installation from the ⁶⁰Co source. The surface density of electret charges σ was calculated by the formula:

$$\sigma_e = \varepsilon \varepsilon_0 \frac{S}{d},$$

where ε is the permittivity of the sample; ε_0 is the dielectric constant; d is the thickness of the sample, and S is the electrode area $\varepsilon_{SiO_2} = 3.9$.

RESULTS AND DISCUSSION

For the analysis of the electret state of polymers, was used an informative and reliable method – thermally stimulated depolarization [8]. The dependence of stabilized electret potentials difference on absorbed dose (D) of the UHMWPE (curve 1) and composite based on it (curves 2–4) are shown in Fig. 1.

$U_{epd}(D)$ dependencies show that for the UHMWPE samples the difference of potential reach the maximum value at $D = 50$ kGy. Further increase in irradiation dose leads to a decrease of the U_{epd} values of the samples. An increase in D up to 100 kGy practically does not affect the values of electrets of UHMWPE+x% α -SiO₂.

We assume that the invariance of U_{epd} of the films containing (1...5%) α -SiO₂ with increasing dose in the

investigated range is due to the fact that most of the electrons generated in each ionization act does not recede beyond the Coulomb field of their ions and recombine with them can participate in the conductivity process.

Comparison of electret characteristics of composites with different composition is correct only in the phase of stabilization of polarization processes.

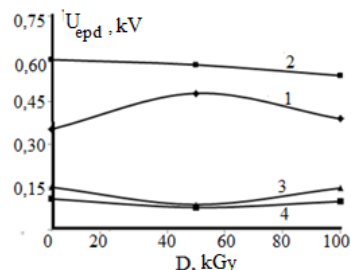


Fig. 1. Dependence of the electret potential difference U_{epd} on γ -irradiation absorbed dose D of the coronoelectret samples: 1 – UHMWPE; 2 – 1 vol.% α -SiO₂; 3 – 3 vol.% α -SiO₂; 4 – 5 vol.% α -SiO₂

Relatively high stability of the electret state in the irradiated UHMWPE+1 vol.% α -SiO₂ composites is probably firstly due to the increase in the degree of crystallinity (lower volume conductivity) of ultrahigh-molecular polyethylene in the composition of the [8] composite film, and secondly, by stabilization of the internal electric field on sub-surface traps that provide a low rate of charge relaxation.

In addition, the filling of UHMWPE can lead to the change in the nature of the supramolecular structure (SMS) of the polymer – the formation of a loosened adsorption layer [19], a decrease in the size of crystallites and spherules [13] which are new nucleating agents.

Therefore in Fig. 2 the dependences of the density of the stabilized electret charges of electrets from UHMWPE (curve 1) and UHMWPE+x% α -SiO₂ composites on the storage time τ_{st} are presented.

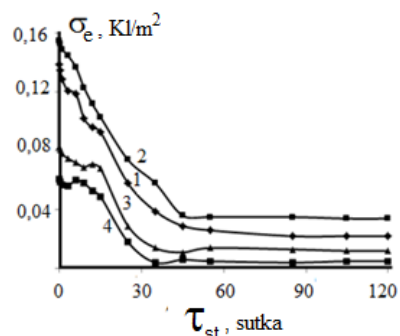


Fig. 2. Dependence of the electret charge density of UHMWPE films and composites on the storage time: 1 – UHMWPE; 2 – 1 vol.% α -SiO₂; 3 – 3 vol.% α -SiO₂; 4 – 5 vol.% α -SiO₂

Studies have shown that the introduction of a filler has a significant effect on the manifestation of an electret effect in UHMWPE: 1% vol. of silicon dioxide in UHMWPE reaches a maximum value, and then decreases (see Fig. 2, curves 3, 4), that is, the best

electret properties of UHMWPE compositions with 1 vol.% of α -SiO₂ content.

The observed increase in σ_e UHMWPE composites (curve 2) is due to the presence of the above-described energy traps and also injected charge carriers which is characteristic for polymer compositions.

One of the characteristics of the electret state of the dielectrics is the electret potential difference U_e of their surface. It depends on the number of injected charge carriers penetrating into the material during the electrification of polymers under the corona discharge.

The stability of the coronolectret mainly depends on which energy traps most of the injected charge carriers fall into—small or deep ones. The curves of the dependence of the σ_e coronolectret on the basis of UHMWPE polyethylene on storage time are shown in Fig. 2.

It can be seen that the electret characteristics of pure UHMWPE and composites based on it on the first day of storage in room conditions are sharply reduced and stabilized by 20...30 days.

This phenomenon is typical for traditional electrets. A sharp decrease in the values of σ_e on the first day of storage is explained by the release of injected charge carriers from small traps, which can be specific surface defects caused by oxidation processes, adsorbed molecules, the short-range order of molecules on the surface and in a volume [20].

The presence of charge carriers in deep traps, which can serve as impurity ions, the phase boundary, the free volume of the polymer, determine the magnitude and stability of the charge of the polymer electret.

To elucidate the reasons for improving the electret state of the UHMWPE+1% α -SiO₂ composition, the TSD spectra were taken. The results of these studies are presented in Figs. 3–5.

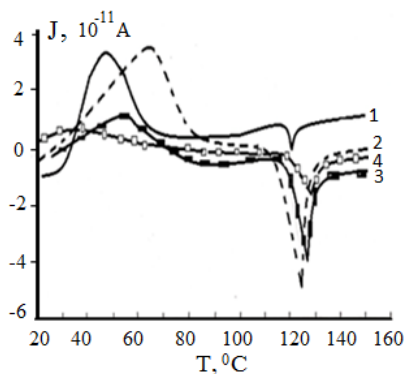


Fig.3. TSD curves of the samples: 1 – UHMWPE; 2 – 1 vol.% α -SiO₂; 3 – 3 vol.% α -SiO₂; 4 – 5 vol.% α -SiO₂

The results of investigations of the currents of the coronolectret of the UHMWPE films before and after the modification by the γ -radiation are shown in Fig. 3.

The spectra of the UHMWPE TSD (curve 1) show two peaks at $(48 \pm 2)^\circ\text{C}$ and a weak maximum at $(116 \pm 2)^\circ\text{C}$. On the spectra of the TSD of the composite with 1 vol.% a nanoparticles α -SiO₂ (curve 2) two peaks are also observed: positive with a maximum at $(65 \pm 3)^\circ\text{C}$ and negative with a maximum at $(125 \pm 3)^\circ\text{C}$.

The first peak can be caused by the movement of weakly bound charges, which causes their relaxation. The second peak corresponding to the softening temperature of UHMWPE is due to the destruction of the main part of the deep traps located at the interface between the crystalline and amorphous phases of UHMWPE.

The spectra of TSD composites with a high concentration of 3 and 5 vol.% of the α -SiO₂ filler also exhibit two maxima at the appropriate temperatures. However, for a composite with 1 vol.% α -SiO₂ nanoparticles, the value of the current of the TSD at a maximum at 125°C is approximately 5 times greater than the peak intensity at 116°C for UHMWPE.

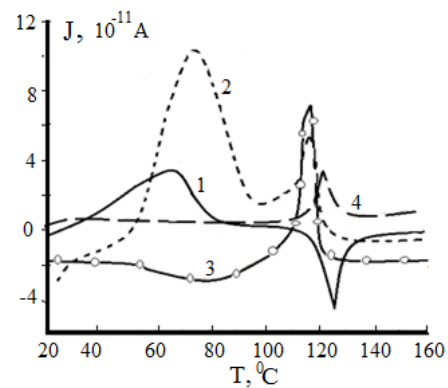


Fig. 4. Curves of TSD for UHMWPE+1 vol.% α -SiO₂ polarized under the corona discharge (1); previously irradiated, and then polarized in the corona discharge (2); pre-electrification in the corona discharge, and then irradiation in air under the action of γ -irradiation (3), and γ -irradiated (4)

Fig. 4 shows the spectra of the currents of the TSD of coronolectret samples from the compositions of UHMWPE+1 vol.% α -SiO₂: 1) subjected to discharge (curve 1, coronolectret); 2) previously irradiated with γ -quanta ($D = 100 \text{ kGy}$) in air; and then polarized under corona discharge (curve 2); 3) previously polarized in the corona discharge zone, and then irradiated in air (curve 3); 4) γ -irradiated samples (radioelectric, curve 4).

It can be seen from Fig. 4 that preliminary γ -irradiation has a noticeable effect on the spectra of the TSD currents (curves 2–4) of the composite:

1) the amplitude of the high-temperature peak of all irradiated composites increases;

2) its shift toward low temperatures by approximately 50°C (absorption dose $D = 100 \text{ kGy}$);

3) after the γ -irradiation, the low-temperature peak practically disappears (curves 3–4) the maximum amplitude of the high-temperature peak is approximately 2 times smaller than the low-temperature peak of the composite UHMWPE+1 vol.% α -SiO₂ (curve 2).

It follows from Fig. 5 that corona electrics from unirradiated ($D = 0$) compositions of UHMWPE+1 vol.% of α -SiO₂ are more stable. Since the stability of electrets is determined by the number of charge carriers in deep volume traps, the low stability of

the γ -irradiated coronelectrode samples can be associated with their increased conductivity and a high rate of charge relaxation.

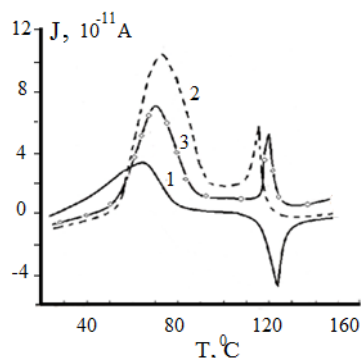


Fig. 5. Curves of TSD for UHMWPE+1 vol.% α -SiO₂ irradiated with a dose of kGy: 1 – 0; 2 – 50; 3 – 100

The nature of the currents of the TSD indicates that the currents of the TSD are mainly associated with near-surface low-energy traps. Consequently, γ -radiation leads to the destruction of deep volume traps at the interfaces between amorphous and crystalline phases and the deterioration of the electret properties of composites [5, 8, 20]. The current of the TSD of the pre-irradiated films proves once again that after γ -irradiation, the charges injected from the corona zone are mainly accumulated in the near-surface layers of the

irradiated samples [8]. Optimum characteristics of nanocomposite corona electrets UHMWPE+1 vol.% α -SiO₂ are shown in the Table.

CONCLUSIONS

1. In this paper, the influence of nanofiller-amorphous α -SiO₂ and the absorbed dose of γ -irradiation on the electret properties of UHMWPE was studied. It was found that with the filling of UHMWPE with silicon dioxide, up to 1 vol.% its electret properties are improved, which is explained by the appearance in the system of new energetically deep traps, injected charge carrier.

2. Introduction of silicon dioxide-into UHMWPE leads to an increase and thermal stability of the composite UHMWPE+1 vol.% α -SiO₂. The low stability of corona electrodes at high doses of irradiation of samples can be associated with their increased conductivity and high rate of charge relaxation. The increase in conductivity with an increase in the percentage of aerosil can be explained by the appearance of additional conductivity over the surface of the filler particles.

3. On the basis of the time dependence of $eI(t_{st})$ of coronelectret samples, it was shown that electrets from the composition of composition UHMWPE+1 vol.% α -SiO₂ irradiated at $D = 50$ kGy are more stable.

Electret characteristics of corona electrets from compositions UHMWPE+1 vol.% α -SiO₂

Sample UHMWPE+1% α -SiO ₂	Dose D , kGy	Max. temperature T_m , °C	Activ. energy U , eV	Charge σ_{el} , C/m ²
Unradiated Coronelectret	0	65	0.014	$38.5 \cdot 10^{-6}$
		125	0.23	$143.0 \cdot 10^{-7}$
γ -irradiated	50	120	0.044	$128.0 \cdot 10^{-6}$
		100	0.21	$240.0 \cdot 10^{-7}$
UHMWPE+1% α -SiO ₂ (coronelectret after preliminary γ -irradiation)	50	75	0.044	$128.0 \cdot 10^{-6}$
		100	0.055	$85.1 \cdot 10^{-6}$
UHMWPE+1 vol.% α -SiO ₂ (coronelectret before preliminary γ -irradiation)	50	70	0.18	$137.2 \cdot 10^{-7}$
		120	0.59	$243.0 \cdot 10^{-7}$
UHMWPE+1 vol.% α -SiO ₂ (coronelectret before preliminary γ -irradiation)	100	118	0.15	$103.0 \cdot 10^{-6}$
		120		

REFERENCES

- I. Pleša, P.V. Notinger, S. Schlögl, C. Sumereder, and M. Muhr. Properties of polymer composites used in high voltage Applications // *Polymers*. 2016, v. 8, p. 173; doi:103390/polym.8050173, www.mdpi.com/journal/polymers, 63p.
- F. Hussain, M. Hojati, M. Okamoto, R.E. Gorga. Polymer – matrix Nanocomposites, Processing, Manufacturing, and Application: An Overview // *J. Comp. Mat.* 2006, v. 40, p. 1511-1575.
- E.G. Selyutin, Yu.Yu. Gavrilov, E.N. Voskresenskaya, V.A. Zakharov, V.E. Nikitin, V.A. Poluboyarov. Composite materials on the basis of extremely-macromolecular polyethylene: properties, prospects of use // *Chemistry for the Benefit of Sustainable Development*. 2010, v. 18, p. 375-384.

- D. Yang. *Advances in nanocomposites – Synthesis, characterization and industrial applications* / Eds. Boreddy S. R. Reddy Rijeka. Croatia: In Tech., 2011, p. 857-882.
- G.N. Churilov, N.G. Vnukovo, G.E. Selyutin, I.V. Osipova. Receiving and a research of composites on the basis of extremely-macromolecular polyethylene and WO₃ // *FTT*. 2009, v. 51, N 6, p. 813-814.
- A.V. Smirnov, B.A. Fedorov, D.E. Temnov, E.E. Fomicheva. Structural and electret properties of polypropylene with various content of amorphous dioxide of silicon // *Nanosystems: Physics, Chemistry, Mathematics*. 2012, N 3(2), p. 65-72.
- R.S. Ismayilova, A.M. Magerramov, M.M. Kuliev, G.A. Akhundova. Electrical Conductivity and Dielectric Permittivity of γ -irradiated Nanocomposites

Based on Ultrahigh-Molecular-Weight Polyethylene Filled with α -SiO₂ // *Surface Engineering and Applied Electrochemistry*. 2018, v. 54, N 1, p. 6-11.

8. M.M. Kuliyeв, A.M. Magerramov, R.S. Ismayilova, A.A. Nabiyeв. Nanocomposite koronoelektreta on the basis of polyethylene of high density and dioxide of silicon // *Perspective Materials*. 2015, N 7, p. 17-22.

9. I.D. Simonov-Yemelyanov, N.V. Aneksimov, A.N. Trofimov, A.Yu. Zolkina, T.I. Andreyeva, O.O. Petrov. Structurization, structures and properties of the disperse filled polymeric composites // *Plastic*. 2012, N 6, p. 7-13.

10. G. Celebiefe, C. Bindal, and A.H. Ucisik. Characterization of UHWPE-TiO₂ Composites Produced by Gelation/Crystallization Method // *Acta Physica Polonica A*. 2017, v. 132, N 3, p. 767-769.

11. V.N. Gud, B.S. Kolupayev, E.V. Malinovsky. Electrophysical properties of the radiation irradiated films of amorphous polymers // *EOM*. 2012, v. 48(2), p. 67-71.

12. A.M. Magerramov, M.M. Kuliyeв, N.A. Aliyev, R.S. Ismayilova, M.N. Bayramov, I.I. Abbasov. Dielectric properties of the composites of polyethylene of high density / ZnO modified by γ -radiation // *Vicnik NTU, HSh*. 2017, N 4 (1266), p. 13-19.

13. A.M. Magerramov. *Structural and radiation modifying of electret, piezoelectric properties of polymeric composites*. Baku, Elm, 2001, 327 p.

14. M. Garcia, G.V. Vliet, S. Jain, B.A.G. Schrauwen, A. Sarkissov, B. Boukamp. Polypropylene/SiO₂

nanocomposites with improved mechanical properties // *Rewviews on Advanced Materials Science*. 2004, v. 50, p. 169-175.

15. E. Kontou, M. Niaounakis. Thermo-mechanical properties of LDPE/SiO₂ nanocomposites // *Polymer*. 2006, v. 47, p. 1267-1280.

16. *Electrets* / Under the editorship of G. Sessler. M.: "World", 1983, 487 p.

17. Yu.A. Gorokhovatsky, L.B. Aniskina, V.V. Burda, M.F. Galikhanov, I.Yu. Gorokhovatsky, B.A. Tazekov, O.V. Chistyakova. About the nature of an electret state in composite films of polyethylene of high pressure with nanodisperse SiO₂ nanofillers // *News of the Russian State Pedagogical University of A.I. Herzen. Physics*. 2009, N 95, p. 63-76

18. Yu.L. Osina, M.F. Borisova, M.F. Galikhanov. Influence of additives of technical carbon on stability of an electret condition of polyethylene of high pressure // *Power. Electrical equipment. Scientific techn. permission*. Sankt-Peterb. goud. Polytechnic University. UNITA. 2013, 4-1(183), p. 151-157.

19. M.F. Galikhanov. Influence of structural parameters of polyethylene on its electret properties // *Plastics*. 2017, N 1-2, p. 14-17.

20. M.M. Kuliyeв, R.S. Ismayilova. The gamma-radiation effect on the spectrum of thermally stimulated current in polyethylene of high density // *Surface Engineering and Applied Electrochemistry*. 2010, v. 46, N 3, p. 447-451.

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ЭЛЕКТРЕТНЫЕ СВОЙСТВА γ -ОБЛУЧЕННЫХ КОМПОЗИТОВ СВЕРХВЫСОКОМОЛЕКУЛЯРНОГО ПОЛИЭТИЛЕНА/ α -SiO₂

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Изучены влияния диоксида кремния (α -SiO₂) и поглощенной дозы γ -облучения на электретные свойства композитов сверхвысокомолекулярного полиэтилена (СВМПЭ)+ α -SiO₂. Установлено, что зависимость стабилизированного заряда от объемного содержания наполнителя α -SiO₂ имеет экстремальный характер: при 1% α -SiO₂ заряд достигает максимума, а затем уменьшается. На основе анализа спектров ТСД показано, что улучшается термостабильность электретов из композита СВМПЭ+1% α -SiO₂. Характер тока ТСД предварительно γ -облученных до доз 50...100 кГр пленок доказывает, что после γ -облучения инжектированные из зоны короны заряды в основном накапливаются в приповерхностных слоях. Ухудшение электретных свойств предварительно γ -облученных композитов связано как с повышением электропроводности, так и с возрастанием скорости релаксации зарядов.

ЕЛЕКТРЕТНІ ВЛАСТИВОСТІ γ -ОПРОМІНЕНИХ КОМПОЗИТІВ НАДВИСОКОМОЛЕКУЛЯРНОГО ПОЛІЕТИЛЕНУ/ α -SiO₂

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Вивчено вплив діоксиду кремнію (α -SiO₂) і поглинутої дози γ -опромінення на електретні властивості композитів надвисокомолекулярного поліетилену (НВМПЕ)+ α -SiO₂. Встановлено, що залежність стабілізованого заряду від об'ємного вмісту наповнювача α -SiO₂ має екстремальний характер: при 1% α -SiO₂ заряд досягає максимуму, а потім зменшується. На основі аналізу спектрів ТСД показано, що поліпшується термостабільність електретів з композиту НВМПЕ+1% α -SiO₂. Характер струму ТСД попередньо γ -опроміненних до доз 50...100 кГр плівок доводить, що після γ -опромінення інжектвані із зони корони заряди в основному накопичуються в приповерхневих шарах. Погіршення електретних властивостей попередньо γ -опроміненних композитів пов'язано як з підвищенням електропроводності, так і зі зростанням швидкості релаксації зарядів.