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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

**STRUCTURE AND ELECTROPHYSICAL PROPERTIES OF
POLYVINYLIDENE FLUORIDE/nano Si COMPOSITES
MODIFIED BY γ -RAYS**

Specialty: **2225.01 – Radiation Materials Science**

Field of science: **Physics**

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GENERAL CHARACTERISTICS OF THE RESEARCH WORK

Relevance of the research topic. In the 21st century, the interest in the acquisition and study of polymer nanocomposites for various purposes, having mechanical, electrophysical, photo-, luminescent and optical properties have greatly increased. Such composites obtained on the basis of polar and non-polar polymers have a wide application area as an active element in various fields of science and technology: transport, space technology, electrical engineering, electrical equipment, insulators and converters and electronic device making. The fillers used to obtain such composites are selected and used in order to improve their physical and technological properties and performance. Composites derived from a mixture of polymers and various chemical components sometimes cause the formation of superior or newer materials. The influence of the filler on the properties of composites depends not only on its concentration, size and degree of distribution in the volume, but also on the interaction of the filler with the polymer matrix. The study of physical and chemical structure, surface activity, electrophysical properties of the individual composite components and electrical charge states of the interphase boundary is very important and urgent issue to clarify the mechanism of interphase interactions in crystallizable polymer-based nanocomposites. Polymer composites with nanometer-size fillers are of great interest. Thus, the acquisition and application of composites with high-chemical and thermal stability on the basis of electroactive polar polymer with the fillers as silicon (Si) having good photocatalytic activity imply their use as nonlinear elements in the solar converters, photo- and optoelectronics, gas sensors and electrical engineering based on their electrophysical and photocatalytic properties.

Polymer nanocomposites can be formed in many ways, from mechanical mixture of components, by mixing nanoparticles with the solution or alloy of polymer, or by polymerization with the presence of nanoparticles. In this case, the compatibility between the phases of the components system is a prerequisite for obtaining homogeneous distribution of the inorganic filler. After all, the properties of the obtained material are determined by the interaction between the matrix and filler phases. Studies show that with the help of various external influences, it is possible to change the interphase interaction and properties of components in composite materials, and to purposefully control, that is, to modify this or other properties of composite. In our dissertation thesis, composites with $(\text{CH}_2\text{-CF}_2)_n\text{-(CF}_2\text{-CF}_2)_m$ monomer structure, obtained on the basis of

polyvinylidene fluoride copolymer with tetrafluoroethylene P(VDF-TePE) with ~ 50 nm and ~ 50 μm size Si particles from polar polymers have been selected as a research object.

Aim of the study: Structural changes in gamma-modified P(VDF-TeFE)/Si composites obtained on the basis of polyvinylidene fluoride copolymer with tetrafluoroethylene P(VDF-TePE) with 50nm nano-Si and ~ 50 μm micro-Si particles and their electrophysical properties have been studied.

Research objects

The following samples have been used as research objects:

- thin films of polyvinylidene fluoride copolymer with tetrafluoroethylene P(VDF-TePE) obtained by thermal pressing;
- thin films of P(VDF-TeFE)/nano-Si and P(VDF-TeFE)/micro-Si composites obtained from mechanical mixture of fine-grained components by thermal pressing;
- thermally pressed thin films of P(VDF-TeFE)/nano-Si and P(VDF-TeFE)/micro-Si composite samples obtained from the solution of Si particles with P(VDF-TeFE) in the solvent by spill (diffusion) method.

The following issues have been resolved to achieve the goal:

- obtaining P(VDF-TeFE)/Si composites based on γ -modified P(VDF-TeFE) copolymer with $d\sim 50$ nm and $d\leq 50$ μm size Si particles in different volume ratios;
- x-ray structural analysis (XSA) of P(VDF-TeFE) copolymer and P(VDF-TeFE)/nano-Si and P(VDF-TeFE)/micro-Si composites obtained on its base;
- study of γ -modified P(VDF-TeFE), P(VDF-TeFE)/nano-Si and P(VDF-TeFE)/micro-Si composites by DTA, TGA, IR and UV spectroscopy;
- comparative analysis of the temperature dependence of a specific resistance (ρ) of the γ -modified P(VDF-TeFE), P(VDF-TeFE)/nano-Si and P(VDF-TeFE)/micro-Si composites, measured in the constant electrical field;
- comparative analysis of the temperature-frequency dependence of electrophysical parameters (ϵ , $\text{tg}\delta$, ρ_v) of γ -modified P(VDF-TeFE), P(VDF-TeFE)/nano-Si and P(VDF-TeFE)/micro-Si composites measured in the alternating electrical field;
- study of a charge state of γ -modified P(VDF-TeFE), P(VDF-TeFE)/nano-Si and P(VDF-TeFE)/micro-Si composites;
- study of luminescent properties of γ -modified P(VDF-TeFE), P(VDF-TeFE)/nano-Si and P(VDF-TeFE)/micro-Si composites;

- analysis of results obtained on the basis of three-phase structure model of crystallizable polymers and the determination of parameters for the modification of composites by gamma rays;

Basic provisions for defense:

1. Possibility of obtaining composites on the basis of micro- and nano-Si by crystallizable polymers;
2. Structural changes caused by gamma radiation in P(VDF-TeFE)/nano-Si and P(VDF-TeFE)/micro-Si composites;
3. Influence of gamma radiation on electrophysical properties of P(VDF-TeFE)/nano-Si and P(VDF-TeFE)/micro-Si composites;
4. Influence of gamma radiation on charge state of P(VDF-TeFE)/nano-Si and P(VDF-TeFE)/micro-Si composites;
5. Role of interaction and gamma radiation at the polymer-filler interphase boundary in formation of electrophysical properties of P(VDF-TeFE)/nano-Si and P(VDF-TeFE)/micro-Si composites.

Scientific innovations.

In the dissertation:

1. It has been determined on the basis of $\lg\rho_v=f(\Phi)$ dependence of P(VDF-TeFE)/Si composites modified by gamma rays up to 300 kGy dose that in the samples obtained by micro-Si, the beginning of the percolation region shifts to higher structures, as the radiation dose increases. However, in the samples obtained by nano-Si, as the dose increases, the beginning of the percolation region decreases monotonically at the measured interval after ~15% value of the filler and the decline rate is slowing down as the dose increases.
3. Correlation between the particle sizes and the values difference of the band gap width (E_g) obtained from the study of P(VDF-TeFE)/nano-Si and P(VDF-TeFE)/micro-Si composites by UV absorption spectroscopy.
4. Comparative analysis of $\lg\rho_v=f(1/T)$ dependence of the initial and irradiated P(VDF-TeFE)/Si composites showed that the reason why the composites obtained with nano-Si are resistant to ionizing radiation is high concentration of nanofiller in the composite volume and more homogeneous distribution.
5. It has been shown that the differences in the frequency dependence of the dielectric parameters of P(VDF-TeFE)/Si composites obtained with nano and micro-Si are due to the high particle concentration in the composites obtained with nano-size Si.

6. It has been shown that active centers, radicals, and structural defects caused by low-dose (~100 kGy) γ -radiation exposure interact with filler particles and increase crystalline β -phase in the P(VDF-TeFE)/nano-Si nanocomposites and cause a decrease in the dielectric parameters by reducing the polymer chain mobility. Irradiation at higher doses (~500 kGy) leads to the beginning of destruction in interphase boundary layer and, consequently, to a slight increase in mobility, as well as dielectric parameters.
7. Comparative analysis of the temperature and frequency dependence of the electrophysical characteristics of the initial and irradiated P(VDF-TeFE)/nano-Si composites obtained from the solution shows that their structural relaxation processes are determined by the ratio of construction and destruction processes in the polymer matrix and interphase boundary.
8. It has been shown that structural changes in P(VDF-TeFE)/nano-Si composites, depending on the size, amount and radiation dose, cause differences in the electrical properties of the composites.

Practical significance of the study.

1. By the method described in the dissertation, it is possible to obtain nanocomposites with nanoparticles of any combination on the basis of other polymers that can be soluble in the solvent.
2. The results of the DTA and TGA studies and electrical measurements show that the modification of P(VDF-TeFE)/nano-Si composites with gamma radiation may result in the formation of materials with higher operating characteristics (with thermal and radiation resistance and insulation properties).
3. Gamma-modified P(VDF-TeFE)/nano-Si and P(VDF-TeFE)/micro-Si composites can be used as an active element of appropriate converters as a material with photosensitive, luminescent and photoelectret properties.

Approval of research results. The main results of the work have been reported and discussed not only in the conferences of the Institute of Radiation Problems of the Azerbaijan National Academy of Sciences, but also in other local and international scientific conferences, including:

The V International conf. "Perspectives of peaceful use of nuclear energy", November 21-23, 2012, Baku; The VIII Rep. Conf. "Radiation Researches and Their Practical Aspects" dedicated to the 65th anniversary of the academician M.K. Karimov, November 20-21, 2013, Baku; VI Russian Conference "Actual Problems of high-energy

chemistry”, October 20-22, 2015, Moscow; International Conference Nuclear and Radiation Physics, September 8-11, 2015, Kurchatov, Republic of Kazakhstan; Republican Scientific Conference on “Macromolecular Chemistry, Organic Synthesis and Composite Materials” dedicated to the 50th anniversary of the Institute of Polymer Materials, October 20-21, 2016, Sumgait; International Scientific Forum NUCLEAR SCIENCE AND TECHNOLOGIES dedicated to the 60th anniversary of the Institute of Nuclear Physics. September 12-15, 2017, Almaty, Republic of Kazakhstan; Proceedings of the III International Scientific and Practical Youth Conference “Creative potential of young people in addressing the aerospace issues” (February Reports 2018), AR NAA, February 12-14, 2018, Baku; LII School PNPI and Youth Conference on Condensed Matter Physics (CMP-2018), March 12-17, 2018, St. Petersburg; LXIX International Conference “NUCLEUS-2019” on nuclear spectroscopy and nuclear structure, Dubna, Russia, 1–5 July, 2019; (ISSN 2522-4352) CONFERENCE PROCEEDINGS Modern Trends in Physics, – 01-03 May, 2019, Baku;

Publications. 8 articles (3 works on abroad and 2 by single author) and 10 theses on dissertation topics have been published.

Structure, volume and main content of dissertation work. The dissertation work consists of an introduction, four chapters, results and a list of references of 165 titles. The total volume of the work is 176 pages, including: 49 pictures and 15 tables.

The introduction is justified by the relevance of the research, and the purpose of the work, the scientific novelty of the obtained results, the theoretical and practical significance, and the provisions for the defense have been presented here.

The first chapter provides detailed information on the structure and electrophysical properties of polyvinylidene fluoride (PVDF) and its copolymers, and on silicon (Si) - another component of the polymer composite, which is the subject of the study. The acquisition of polymer - semiconductor based composites and modification of their electrophysical properties by ionizing radiation were considered. The analysis of the scientific literature sources shows that the polymer composites obtained by nano-Si particles have been poorly studied, and the effect of ionizing radiation on these composites has not almost been investigated. The obtained result indicates that research in this field is still relevant. Although

a review of the scientific literature covers the recent achievements of radiation physics and chemistry of polymers and some composites, the effect of ionizing radiation on polymer-based nanocomposites is a little studied field.

The second chapter describes the technology of obtaining P(VDF-TeFE)/Si micro- and nanocomposites by thermal pressing of the mechanical mixture of P(VDF-TeFE)/Si composite components and the mixture obtained from their solution in the solvent and provides preliminary information about the components. Furthermore, the study of nanocomposites by IR and UV spectroscopy, XSA, DTA, RTL and TGA methods are described in this chapter. Methods for γ -radiation on nanocomposites and measurement of their electrophysical properties, electropolarization by corona discharge method, and the study of charge state by thermosimulated depolarization method, and the description of appropriate experimental devices are also covered in this chapter.

In the third chapter, structural changes of composites obtained on the basis of P(VDF-TeFE) copolymers with Si particles and modified by γ -radiation were studied using IR spectroscopy, DTA, TGA, XSA and RTL methods. The application of these methods allows us to obtain valuable information on the structure of polymers and composites, the differences in amorphous and crystalline phases, and the interphase interaction between the components. Structural changes in the composites, caused by gamma-radiation were defined based on the results of comparative analysis of IR spectra before and after radiation (Figure 1). The results of the analysis are presented in Table 1.

In order to evaluate the structural changes in the P(VDF-TeFE)/nano-Si composite, we used the results of change of place and intensity (maximum area) of the C=O carbonyl groups, corresponding to the 1710-1740 cm^{-1} range in the IR spectra of the initial and irradiated composite samples. After radiation exposure, double C=C and C=O carbonyl groups are formed in the IR spectrum of P(VDF-TeFE)/1.0% nano-Si samples. The formation of these groups is manifested in the intensity increase of the absorption band in the range of 1720-1740 cm^{-1} wavenumber in the spectrum. The peaks intensity of the oscillation of C=O carbonyl groups increases as the radiation dose increases.

The increase kinetics of the peak intensity around the 1725 cm^{-1} wavenumber, depending on the absorbed dose strength is quite high.

Table 1.

The change in the intensity (I) for Si-C ($761 \pm 5 \text{ cm}^{-1}$), Si-O-Si ($1075 \pm 10 \text{ cm}^{-1}$), Si-O-C (1069 and 1086 cm^{-1}) and C=O (1710 - 1740 cm^{-1}) bonds in the IR spectra of the initial and irradiated P(VDF-TeFE)/1.0% nano-Si samples

D, kGy			0	100	300	500
	K, cm^{-1}	Φ , volume%	I	I	I	I
1	761	~ 1.07	0.739	1.68	2.82	3.47
2	1075 ± 10	~ 1.07	9.61	37.39	69.1	21.2
3	1710-1740	~ 1.07	2.6	14.83	34.9	52.7

We assume that this is due to the structural changes in the polymer at lower values of Si concentration and the faster formation of C=O carbonyl groups as a result of subsequent oxidation processes. During gamma irradiation, the electron avidity of fluorine in the main chain of the polymer leads to the break of C-F bonds and the reduction of CF_2 groups and the conversion of some of them into $\dot{\text{C}}\text{F}$ radicals. The recombination of these radicals in the matrix results in the formation of inter-chain constructions. It has been established that inter-chain constructions enhance the polymer matrix stiffness, and the interaction of the active centers formed after radiation results in the increase of crystalline phase due to the increase of Si-O-C (1069 and 1086 cm^{-1}) and Si-C (761 cm^{-1}) bonds along with the Si-O-Si ($1075 \pm 10 \text{ cm}^{-1}$) bonds at the matrix-nanoparticle interphase boundary. The increase of intensities of the 509 cm^{-1} and 840 cm^{-1} absorption bands, characterizing the crystalline β -phase in the matrix in IR spectrum of the P(VDF-TeFE)/nano-Si system is the evidence to this. For P(VDF-TeFE)/1% nano-Si samples, the intensities of both Si-O-Si and Si-O-C (1069 and 1086 cm^{-1}) bonds decrease passing from the peak at 300 kGy by the increase of dose. There is observed a decrease in Si-O-C (1069 and 1086 cm^{-1}) bonds and an increase in Si-C (761 cm^{-1}) bonds and in corresponding intensities by the increase of dose up to 500 kGy. IR spectroscopy studies show that the crystallinity degree of the system increases due to the interaction of the active centers formed after radiation in the matrix with the surface of Si nanoparticles at the interphase boundary. The optimal change in optical properties of P(VDF-TeFE)/nano-Si composites depending on the amount of filler and radiation dose falls to the

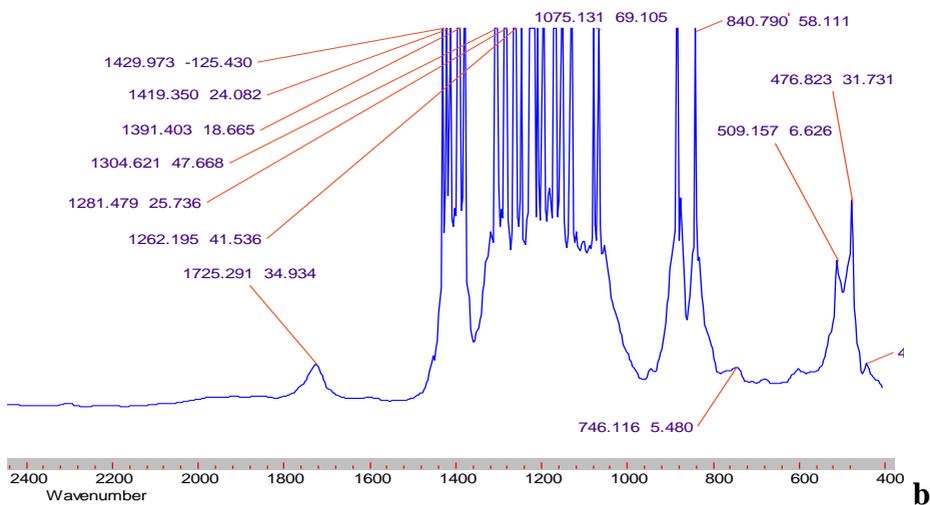
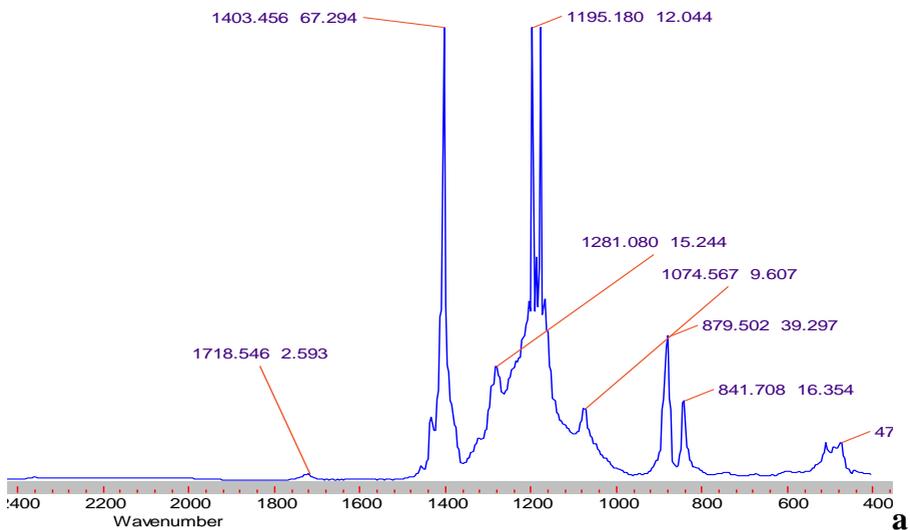


Figure 1. IR spectra obtained before and after gamma radiation of P (VDFTeFE)/nano-Si composites: a- D=0; b- D=300 kGy;

dose range of 100-300 kGy.

Studies of composites using the DTA and TGA methods also yielded similar results. The results of spectra analysis obtained by differential thermal analysis (DTA) of P(VDF-TeFE)/nano-Si composites obtained in different compositions and modified with initial and gamma radiation, and the values of melting endothermic peak temperature (T_m) and enthalpy (ΔH) are given in the Table 2. If we take the value of enthalpy (ΔH) as a qualitative indicator of inter-molecular and interphase bonds in the matrix, then its lowest values can be considered equivalent to the weakening of these bonds, and its highest value to the strengthening. It can be said from the comparison of the values of enthalpy (ΔH) shown in Table 2 that while the value is close for the low-content composites, this value decreases in the high-content of the filler. Therefore, we can say that composites, containing 1-5% nano-Si in volume, have more optimal structure and are more homogeneously distributed in the matrix. As it is shown from Table 2, the value of enthalpy (ΔH) remains constant within the error with the change of the filler in the range of 1-5% in the composite. Thus, as the parameters of interphase boundary layer are higher in a low-content (1–5%) composite, ΔH becomes higher, i.e. polymer-filler bonds become stronger. Subsequent growth of the filler weakens the intermolecular interaction due to the mechanical destruction of the polymer chains, and the clustering of Si particles results in the reduction of the effective surface and in the weakening of the polymer-filler interaction. For the irradiated P(VDF-TeFE)/nano-Si composites, the comparison of table values of enthalpy (ΔH) suggests that the enthalpy slightly decreases or is stabilized after the increase in the compositions containing 5% nano-Si.

Table 2. The value of some parameters of initial and irradiated P(VDF-TeFE)/nano-Si composites obtained from the DTA spectra, endothermic peak temperature (T_m) and enthalpy (ΔH).

№	Composition, volume%	Initial samples		Irradiated samples, D=100 kGy	
		T_m , °C	ΔH , mC/mg	T_m , °C	ΔH , mC/mg
1	1.0	145	25.6	147.5	25.3
2	4.8	145.5	25.5	146.5	28.3
3	12.7	149	23.2	147.5	27.8

This is, on the one hand, due to the homogenous distribution of gamma radiation energy among the nanoparticles, along with the inter-molecular and interphase constructions at the polymer-filler boundary, occurring in polymer matrix, on the other hand, due to the change of properties of nanoparticles after radiation. We consider that structural changes that occur in the components of the P(VDF-TeFE)/nano-Si composite and at the interphase boundary after gamma radiation, are the factors that govern their mechanical and physical (thermal) properties.

The comparative analysis of the thermogravimetric analysis (TGA) spectra of the initial and irradiated P(VDF-TeFE)/1% nano-Si and P(VDF-TeFE)/12.7% nano-Si composites also prove our results. Table 3 shows the values of parameters (Δm , %; ΔT , °C; $\Delta m/\Delta T$, and Δm_{res} etc.) calculated on the basis of various data obtained from the thermodestructive region of the TG spectra of P(VDF-TeFE)/1% nano-Si and P(VDF-TeFE)/12.7% nano-Si composites, ie. from the region where the mass changes sharply depending on the temperature.

According to the TGA spectra of the initial P(VDF-TeFE) copolymer, thermal degradation begins after approximately $T=440^{\circ}\text{C}$ and continues to a temperature of $\sim 490\div 500^{\circ}\text{C}$. The polymer matrix loses most of its mass around this temperature.

Table 3

The values of parameters (Δm , %; ΔT , °C; $v=\Delta m/\Delta T$, %/min and Δm_{res} , % measured at 540°C) calculated from the TGA spectra of P(VDF-TeFE)/1% nano-Si and P (VDF-TeFE)/12.7% nano-Si composites.

Φ , volume %	D , kGy	Δm , %	ΔT , °C	$v=\Delta m/\Delta T$, %/min.	Δm_{res} , % (540°C)
0	0	58.5	53	1.10	26.6
1 (nano)	0	64	32.2	1.99	32
	100	58.4	37.5	1.56	33.7
	300	52	46	1.13	40.5
12.7	0	68	23	2.96	29
	100	60.8	38.7	1.56	35.9
	300	57	51.2	1.11	39.6
1 (micro)	0	62.7	25.8	2.43	21.6

On the other hand, the comparison of parameters obtained before and after the influence of γ -rays on the composites shows that as the radiation dose

increases, there is observed a decrease of decomposition rate ($v=\Delta m/\Delta T$) and an increase of mass residue ($\Delta m_{\text{residue}}$) for both P(VDF-TeFE)/1% nano-Si and P(VDF-TeFE)/12.7% nano-Si composites after the destruction. The reason for this is that the nano-Si particles used as fillers are more evenly distributed in the matrix and behave as crystallization centers, and the amount of crystalline phase increases in the composite, which can be regarded as a structural change. Thus, after the ionizing radiation, the increase of construction processes in the polymer matrix and interphase interactions at the polymer-filler boundary result in the increase of amorphous phase stiffness and the formation of new crystallites.

The spectra of the polymer/nano-Si composites obtained by radiothermoluminescence (RTL) method also confirm what we said (Figure 2). If we carry out the comparative analysis of RTL spectra of P(VDF-TeFE)/Si composites obtained by P(VDF-TeFE), nano- and micro-Si, we shall observe that (Figure 2, curve 2) the peak (β -relaxation), equivalent to the glass transition temperature shifts to lower temperatures compared with the polymer peak in the samples obtained by micro-Si (Figure 2, curve 1). But, these peak shifts to higher temperatures than the polymer in the RTL spectrum of the samples obtained with nano-Si (Figure 2, curve 3). The differences between the RTL spectra of the micro- and nanocomposites are due to the differences in their structure.

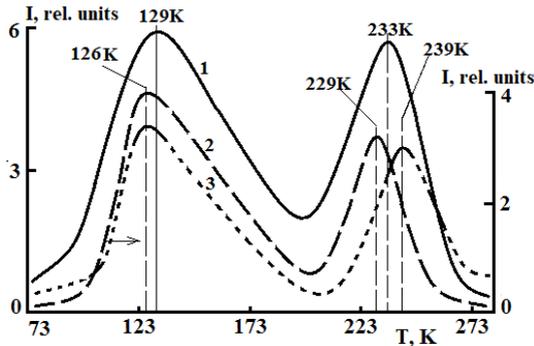


Figure 2. RTL spectra of composites obtained with P(VDF-TeFE), nano- and micro-Si: 1- P(VDF-TeFE); 2- P(VDF-TeFE)/1%micro-Si; 3- P(VDF-TeFE)/1% nano-Si

An increase of particle concentration in the unit volume leads to the increase of a polymer-filler effective surface and crystalline phase in the

matrix, and to the strengthening of interphase interaction, that results in the shift of the β -peak to higher temperatures in RTL spectra of P(VDF-TeFE)/nano-Si composites.

These results are confirmed in diffractograms obtained from the X-ray structural analysis (XSA) of the P(VDF-TeFE)/nano-Si composite. It has been shown that there is a localized state of motion limited by the presence of the nanofiller of macromolecules at the polymer-filler interphase boundary in composites obtained in the low amounts of filler, and the macromolecules are placed regularly, that is, the crystalline regions are generated around the nanoscale particles. It is assumed that a relative decrease of the intensity of new reflexes observed in the diffractograms of composites obtained by nano-sized Si and the wide half width indicate that the sizes of crystallites formed in this region, namely at the interphase boundary, are small. The structural changes that we observed provide an indication that the crystalline phase and exploitation properties of the composite materials, that is, their mechanical and thermal stability have increased.

The fourth chapter discusses the results of the study of electrophysical properties of composites obtained on the basis of Si particles with P(VDF-TeFE) copolymers and modified by gamma rays. Composites of mechanical mixture of P(VDF-TeFE) copolymers with different size silicon (Si) particles were obtained at different volume ratios, their optical properties and dependence of specific electrical resistance on the filler (Si) concentration have been investigated (Figure 3). Dependencies (Figure 3) show that a change in the volume amount of filler up to 50% in the composite results in a non-monotonic change of specific resistance (ρ_v) to ~ 5 , which is typical for heterogeneous composite systems. But, this range does not have a sharp boundary, and the resistance increases monotonically to ~ 3 by the increase of volume amount of filler up to 50% for the composites obtained with nanoscale fillers.

The dependence [$\lg \rho_v = f(\Phi)$] of specific volume resistance of P(VDF-TeFE)/Si composites, initial and irradiated at different doses and obtained on the basis of $d < 50 \mu\text{m}$ (a) and $d \sim 50 \text{nm}$ (b) size fillers, on the concentration of filler has been presented in the figure (Figure 3, a and b). It can be seen that in the gamma-irradiated P(VDF-TeFE)/micro-Si samples, a percolation transition range increases approximately twice as the radiation dose (D) increases and the beginning of percolation transition shifts to the higher values of filler. It is assumed that the observed effect is due to the oxidation of the filler and the construction processes between the

macromolecules of the polymer matrix and between the surface of the Si particles and the polymer macromolecules.

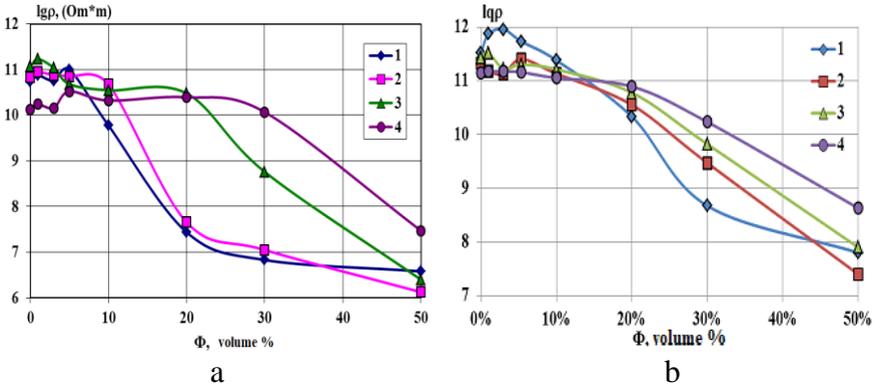


Figure 3. $\rho=f(\Phi)$ dependence of P(VDF-TeFE)/nano-Si composites, initial and irradiated at different doses and obtained on the basis of $d<50\mu\text{m}$ (a) and $d\sim 50\text{nm}$ (b) size fillers: 1- initial, 2- 100 kGy; 3- 200 kGy; 4- 300kGy;

We see that the $\lg\rho_v=f(\Phi)$ dependence of P(VDF-TeFE)/nano-Si composites, initial and irradiated at different doses and obtained on the basis of $d\sim 50\text{nm}$ fillers is different compared to the samples obtained with micro-Si. In these samples, the transition from high-resistance state to low-resistance occurs more rapidly and there is no sharp boundary of percolation transition by increasing filler amount. The reason for this is an increase of the effective field of the interphase polymer-Si boundary proportionally to the increase of filler volume up to $\Phi=50\%$. Here, the reason for the change in the resistance value is the oxidation of the surface of the nano Si particles having a larger effective surface, along with the inter-chaine construction occurring under the influence of radiation in the polymer matrix.

A comparative analysis of temperature dependence ($\lg\rho=f(1/T)$) of specific resistance of P(VDF-TeFE)/Si composites obtained with micro- and nano-size Si particles and modified by γ -rays has been conducted and interesting results have been obtained (Figure 4).

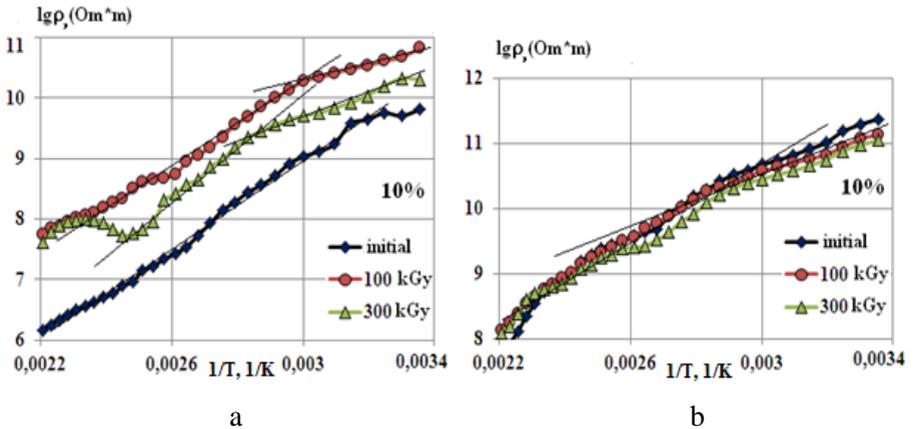


Figure 4. $\lg\rho=f(1/T)$ dependence of P(VDF-TeFE)/Si composites obtained with micro-Si (a) and nano-Si (b) irradiated at different doses.

As it is seen from the $\lg\rho=f(1/T)$ dependence of P(VDF-TeFE)/10%Si composites, the curves of the samples modified at each three doses by the transition from microparticles to nanoparticles coincide with a minor error. The reason of this on the one hand is the increase of interaction between the polymer-filler interphase boundary by the increase in the effective surface of filler, on the other hand, the even distribution of nanosize filler in the volume and more effective absorption of adsorbed dose by the filler due to the high concentration and as a result a decrease of the effect of radiation on the matrix. A decrease in the polymer chains mobility due to the constructions between macromolecules and at the polymer-filler boundary after gamma radiation is one of the factors that allow the special resistance to remain stable. Finally, we can say that the reason why P(VDF-TeFE)/10% nano-Si composites are resistant to gamma radiation is a high concentration and homogeneous distribution of nanoparticles in the composite volume in the same volume amount of filler than the microparticles.

Comparative study of the temperature-frequency dependence of dielectric properties of composites obtained on the basis of micro- and nano Si is also presented in this chapter. It can be studied the relaxation processes occurring in the system and described the interactions in polymer matrix and polymer-filler interphase boundary by conducting a comparative analysis of dielectric parameters (ϵ , $\text{tg}\delta$ and ρ) of composites irradiated at different doses. We have analyzed the influence of modification by γ -rays

on the dielectric properties of nanocomposites according to the $\epsilon=f(D)$ dependence of the samples (Figure 5). As it is seen, while the peak of the ϵ change (extreme change) due to the radiation occurs around 200 kGy value of dose for the initial polymer, this occurs around 100 kGy dose in the composites obtained with nano-Si, ie the dose is nearly halved.

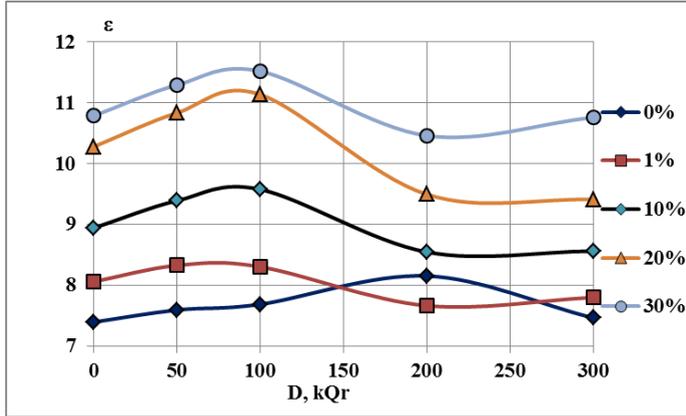


Figure 5. Dependence of dielectric permittivity of P(VDF-TeFE)/nano-Si composites obtained at different volume ratios and measured at room temperature, on radiation dose.

The reason of this is that, although, the constructions between the polymer matrix and nano-Si surface decrease the mobility of the polymer chain and accordingly dipoles around the 100 kGy dose in the composite state, the Maxwell-Wagner polarization, occurring in the volume and polymer-Si interphase boundary, of volume charges formed under gamma-radiation influence in the matrix and filler, is getting stronger. A comparative analysis of the $\lg\rho=f(1/T)$ dependence of initial and irradiated P(VDF-TeFE) polymers and P(VDF-TeFE)/1% nano-Si composites, established in the Arrhenius coordinates measuring at varying voltages, confirms what we said above (Figure 6). In the $\lg\rho=f(1/T)$ dependence established in the Arrhenius coordinates, the number of rectilinear parts in the descent region of the resistance indicates the relaxation processes occurring in the measured samples.

There are some rectilinear regions having different curves in $\lg\rho=f(1/T)$ dependence of the initial (Figure 6, curve 1) and gamma-

irradiated (Figure 6, curves 2-4) P(VDF-TeFE)/1% nano-Si composite samples.

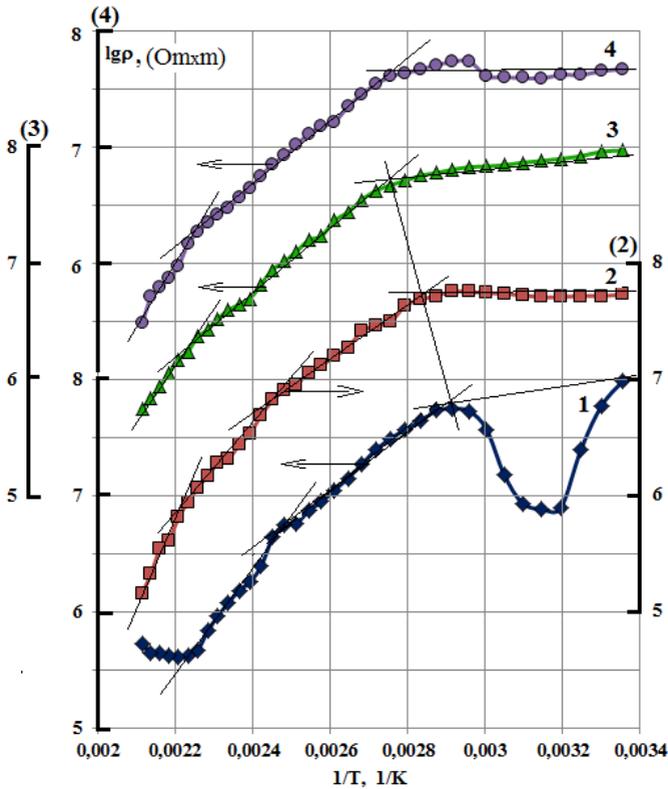


Figure 6. $\lg\rho=f(1/T)$ dependence of P(VDF-TeFE)/1% nano-Si composite measured at variable voltage; 1– initial; 2– 100 kGy; 3– 300 kGy; 4– 500 kGy;

We think, the first curve, is due to the relaxation of dipoles in the polymer matrix. The second curve in the $\lg\rho=f(1/T)$ dependence of P(VDF-TeFE)/1% nano-Si composite is related to the increase of molecules mobility in interphase layer, in accordance with the 3-phase model of crystallizable polymers, between polymer matrix and nano-Si surface, and the release of the charge accumulated at the interphase boundary. It can be seen from the dependence that there is observed the stabilization and

increase of special resistance defined by the nano-Si conductivity, in the high temperature region in the $\lg\rho=f(1/T)$ dependence of initial P(VDF-TeFE)/1% nano-Si composite. Quite vertical third curve is observed in this temperature range in gamma-irradiated composites. We consider that in the $\lg\rho=f(1/T)$ dependence of P(VDF-TeFE)/1% nano-Si composite, the last, vertical curve observed in the high temperature region is the result of destruction in the polymer and increase in the nano-silicon conductivity.

There is observed a minimum of resistance due to the desorption of the absorbed moisture (water) at low temperature region (293-343K) in the $\lg\rho=f(1/T)$ dependence of the initial P(VDF-TeFE)/1% nano-Si composite. This minimum is not observed in the $\lg\rho=f(1/T)$ dependence of irradiated P(VDF-TeFE)/1% nano-Si composite samples. The reason for this is the construction processes between silicon nanoparticles and polymer matrix at the interphase boundary and between the polymer matrix chains after irradiation. On the other hand, it is seen that in $\lg\rho=f(1/T)$ dependence of the samples modified with the irradiation dose of 100 and 300 kGy, the beginning of fall shifts 15–20 K to high temperatures in the higher temperature region. In samples irradiated at 500 kGy dose, we see that the temperature corresponding to the beginning of the fall is already stabilized. Thus, we can say that this ~15–20 K temperature shift can be considered as the improvement of operational features of composite by the modification with γ -radiation and the 100 kGy dose as a modification dose.

It is possible to make some idea about the parameters of the charge capture centers by the polarization of polymer composites through corona discharge method, then the study of spectrum of thermoderolization (TSD) currents. It is known that the charge state of polar polymers depends on the dipole mobility and the localization level of the charge capture centers in the band gap, that is, on the concentration and energy depth of the traps on the surface and volume of the material. By controlling these parameters, it is possible to obtain materials with supramolecular structure having different characters based on polymer composites with the same composition. The modification of composites by ionizing radiation is characterized by the change in their structural parameters and charge state. On figure 7 shows the changes in the TSD spectra of P(VDF-TeFE)/nano-Si composites depending on the absorption dose rate of the gamma radiation. As it is seen from the figure, there is three peaks in the TSD spectra of P(VDF-TeFE)/1% nano-Si composites (Figure 7, a) at the temperature range of 353-373 K, 423-443 K and around 463 K. The peak with relatively low temperature among these peaks is generated by thermal

relaxation of dipoles of the P(VDF-TeFE) matrix, as other authors have said. Subsequent peak (353-373 K) and (423-443 K) are, in our opinion, the result of the relaxation of charges in the interphase layer between crystalline and amorphous phase of polymer and at the polymer-filler interphase boundary, i.e., Maxwell-Wagner polarization at the interphase boundary.

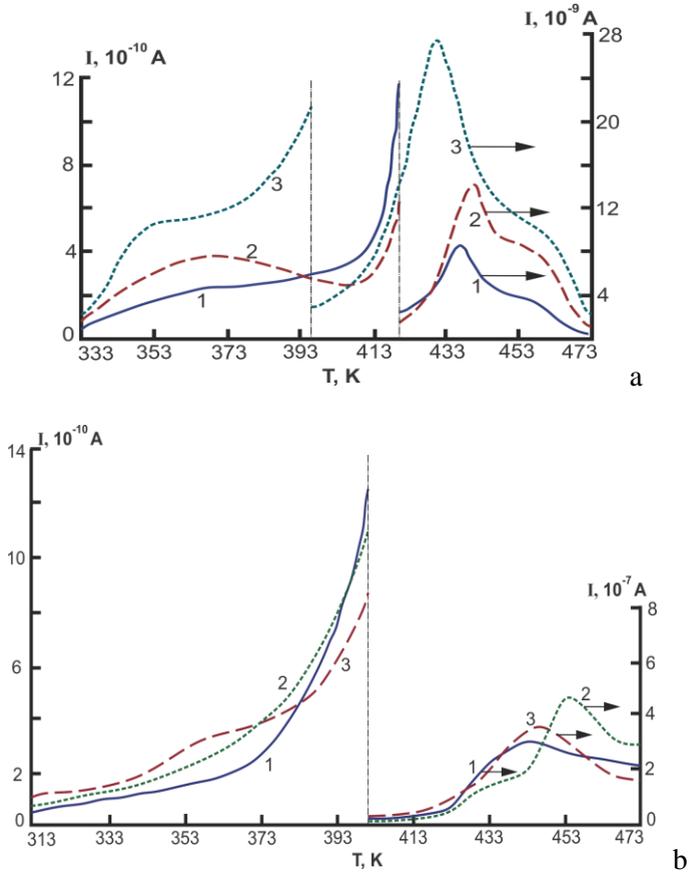


Figure 7. TSD spectra of P(VDF-TeFE)/nano-Si composites obtained at different volume ratios and modified with gamma rays: a- P(VDF-TeFE)/1% nano-Si; b- P(VDF-TeFE)/10% nano-Si; 1- initial; 2- 100 kGy; 3- 300 kGy

The spectra, we believe, confirm the correctness of the explanation for the changes in electrophysical properties. If we look at the dependence of the high-temperature peaks on absorption dose of gamma radiation in the spectra of the composites obtained in both volume ratios, we can see that the peak belonging to the matrix in the composite with the 100 kGy dose, first of all, shifts to high temperatures than the peak of initial sample, but it shifts to relatively low temperatures again when the dose increases up to 300 kGy. In our opinion, the reason for this is the increase in the construction process between the macromolecules of the polymer matrix at the dose of 100 kGy. The macromolecules that are subjected to the construction shift to higher temperatures as they need more energy to obtain mobility. When the dose rate rises to 300 kGy, it is likely that the beginning of the destruction processes increases the release degree of macromolecules, and we also observe the displacement of the peak to the reverse.

Comparative analysis of the current value of peaks also confirms that. Comparing the parameters of the peak around ~463 K, we observe a shift to higher temperatures as the dose increases, which indicates that the interaction between the polymer matrix and Si nanoparticles increases as the dose increases and more charges accumulate at the interphase boundary. Furthermore, we see that the increase in the volume amount of nanoparticle up to 10% (Figure 7, b) also results in an increase in the accumulated charge due to the increase on the interphase effective surface. The amount of charges in the interphase layer between crystalline and amorphous phase of polymer is more in composites where nanoparticles contain 1%, while the relaxation of charges at the polymer-filler interphase boundary prevails in the composite where nanoparticles contain 10%. In this part of the spectra, a shift of corresponding peaks to high temperatures can be regarded as an increase in activation energy of charge capture centers, i.e. an increase in the concentration of higher-energy levels depending on the dose rate and the filler amount. As it is seen from the TSD spectra of these composites, the higher temperature and intensity corresponding to the peak of the sample modified at 100 kGy dose and enough charge at the 473K temperature confirm again that this dose is the modification dose for these composites.

MAIN RESULTS

1. It has been determined according to the $\lg\rho=f(\Phi)$ dependence of P(VDF-TeFE)/Si composites exposed to gamma radiation up to 300 kGy dose range that for the samples obtained by micro-Si, the percolation region shifts to higher structures as the radiation dose increases. However, for the samples obtained by nano-Si, the percolation region extends as the dose increases and the change rate of resistance decreases in this region. In both cases, the reason for this change is the oxidation of Si particles surface due to radiation and the increase of polymer-filler interaction.
2. It has been shown that active centers, radicals and structural defects caused by gamma radiation at $\sim 100\div 300$ kGy dose lead to the decrease in the polymer chain mobility in P(VDF-TeFE)/nano-Si nanocomposite and the increase in special electrical resistance by interacting with nanostructures. $D\geq 500$ kGy dose radiation results in a slight decrease in the resistance as a result of destruction of polymer matrix and interphase boundary layer.
3. The bonds of Si-O-C (~ 1069 vø 1086 cm^{-1}) and Si-C (~ 761 cm^{-1}) in the IR spectra of the initial and irradiated P(VDF-TeFE)/nano-Si composites, new reflexes ($14,5^\circ$; $16,6^\circ$; $21,2^\circ$; $22,5^\circ$; $23,1^\circ$) in X-ray diffractograms, and the displacement of the β maximum to high temperatures in the RTL spectra indicate the formation of a polymeric layer with a different structure at the interface. Parameters of these layers determine the electrophysical properties of the composite.
4. Comparative analysis of the temperature and frequency dependence of electrophysical properties of the initial and irradiated (P(VDF-TeFE)/nano-Si composite obtained from the solution shows that the relaxation processes are determined by the ratio of construction and destruction processes in the polymer matrix and interphase boundary.
5. It is shown that in the IR spectra of P(VDF-TeFE)/nano-Si composites, there is a certain correlation between the change in the intensity of bands of Si-O-C (~ 1069 and 1086 cm^{-1}) and Si-C (~ 761 cm^{-1}) bonds, along with the Si-O-Si ($\sim 1075\pm 10$ cm^{-1}) bonds, depending on the amount of filler and radiation dose and the change in the special resistance (ρ_v) of composites.
6. It has been determined the increase to $\sim 15\text{-}20^\circ\text{C}$ in thermal resistance of (P(VDF-TeFE)/nano-Si composites obtained in the $1\div 10\%$ volume amount of filler and modified at 100 kGy dose and (P(VDF-

TeFE)/10% nano-Si containing composite to be resistant to γ -radiation up to 300 kGy. It seems that the dose of ~ 100 kGy is the optimal modification dose for composites, which improves their operational properties.

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