

## THE INFLUENCE OF GAMMA IRRADIATION ON ELECTRIC PROPERTIES OF POLYVINYLIDENE FLUORIDE COMPOSITES WITH SILICON

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The influence of gamma irradiation up to dose 300kGy on electric properties of polymer composites on the base of copolymer of polyvinylidene fluoride with tetrafluoroethylene P(VDF-TFE) and micro- and nano-particles of silicon is studied. It is shown that observable changes in electric properties of irradiated composites on the base of P(VDF-TFE) with micro- and nano-particles of silicon are connected with both processes of radical formation and oxidation with further cross-linking and destruction in heterogeneous system and redistribution of absorbed dose of radiation energy between components of composite.

**Keywords:** P(VDF-TFE), micro- and nano-particles of silicon, polymer composite, electric properties, gamma irradiation, temperature dependence of specific resistance, mobility, interface.

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### INTRODUCTION

The introduction of different fillers with specific properties in polymer materials is the one of effective methods of electric property modification of polymer materials to use in electronics. The composite materials obtained by such modification acquire the different active properties in dependence on filler type and properties [1-5]. Moreover, the composite acquired properties can be modified by external influences including the ionizing radiation [6-9]. The study of scientific literature shows that composites with semiconductor inclusions are of large interest. According to supposition of authors of these works, the current value in composites is defined by distance of interparticle isolating layer and VAC of samples forms because of electron tunneling through this composite interlayer. The influence of gamma irradiation on electric properties of composites on the base of copolymer of polyvinylidene fluoride with tetrafluoroethylene P(VDF-TFE) with different content of micro- and nano-particles of silicon (Si) is also investigated in the given work.

### EXPERIMENTAL PART

The composites are obtained by hot pressing method of previously mixed powders in definite volume component ratios. The pressing is carried out at melting point of polymer matrix under pressure 10MPa during 5 minutes with further melt cooling by the deeping way in aquatic environment at ice temperature. The resistance measurement of composite samples is carried out by E6-13A teraohmmeter at heating rate 2K/min. The samples in "sandwich" form with plane-parallel electrodes from aluminum are used for measurement of  $\rho_v$  specific volume resistance.

### RESULT DISCUSSION

The composite temperature dependences of  $\rho_v$  resistivity are investigated for study of kinetics change in conduction process taking place before and after

irradiation exposure in composites with different filler content. Temperature dependences  $\lg \rho = f(1/T)$  of initial and irradiated polymer P(VDF-TFE) are shown in fig.1. It is seen that  $\rho_v$  values of initial and irradiated polymer monotonously decrease but some stabilization of  $\rho_v$  value with further decrease is observed in average temperature range (363-393K) for irradiated samples.

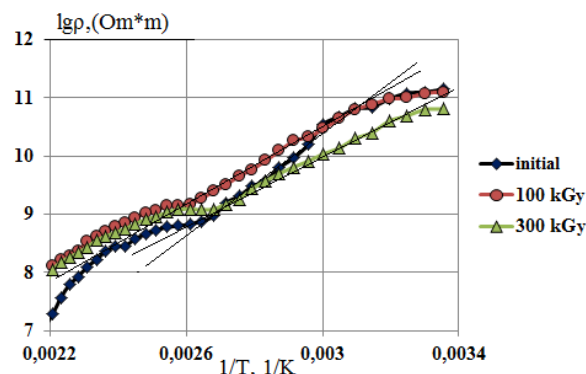
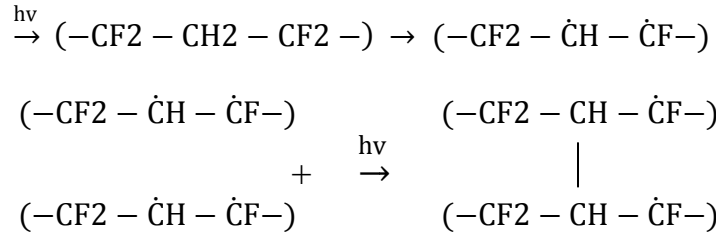


Fig.1. The temperature dependences of volume specific resistance of P(VDF-TFE) polymer irradiated by different dose.

The insignificant decrease of curve inclination angle in comparison with one of initial P(VDF-TFE) is observed in temperature dependence of irradiated polymer samples. We think that the decrease of P(VDF-TFE) polymer chain mobility as a result of carrying out cross-linking after gamma irradiation causes to fact above mentioned. Moreover, irradiation by high doses leads to shift of initial value increase of  $\lg \rho = f(1/T)$  to the side of low temperatures connected with destruction beginning of some weakly bound molecular units of polymer chain. As it is known from [12,13] the ionizing irradiation of fluorine-containing polymers is accompanied by decrease of  $\text{CF}_2$  group number which transform into polymer radicals  $\dot{\text{C}}\text{H}$  and  $\dot{\text{C}}\text{F}$ . As a result, the part of radicals in polymer structure leads to formation of inter-chain cross-linking because of recombination on following scheme:



The intra-chain transversal cross-linking because of presented reaction is accompanied by increase of polymer matrix hardness and decrease of molecular chain mobility in interphase interlayer.

From comparison  $lg\rho = f(1/T)$  dependence for composites with Si micro-particles (fig.2a) it is seen that inclination angle of curves in low-temperature region changes with radiation dose and filler content increasing. The some stabilization (1%Si) and increase with decrease (5 and 10%Si) of  $\rho_v$  value are observed in high-temperature dependence part in region below melting point of polymer matrix. We think that high volume contents and radiation doses (300kGy) lead to increase of radical relative concentrations and volume bound charge number in polymer matrix. At high temperatures the radical recombination taking place with volume free charges in matrix leads to relatively rapid decrease of composite  $\rho_v$  value. The further stabilization and decrease

of  $\rho_v$  are the result of saving properties structure of polymer-filler interface, which destroys at composite melting as a whole.

Stabilization of  $\rho_v$  for samples with 1% volume content observable in high-temperature part of  $lg\rho = f(1/T)$  composite dependence shifts to relatively wide maximum for composites with 3,5 and 10% filler volume content at radiation high doses (~300KGy). The processes of free charge capture by radicals (defects and energy traps) together with cross-linking processes take place at irradiation of samples [14,15]. The inverse mechanism leading to charge release takes place at heating. Besides, radical oxidation can lead to radical trap destroy accompanying with charge release from them and increase of sample electric conduction. But values of accumulated charges aren't endless ones and the some  $\rho_v$  increase taking place after its minimum value at high temperatures is observed.

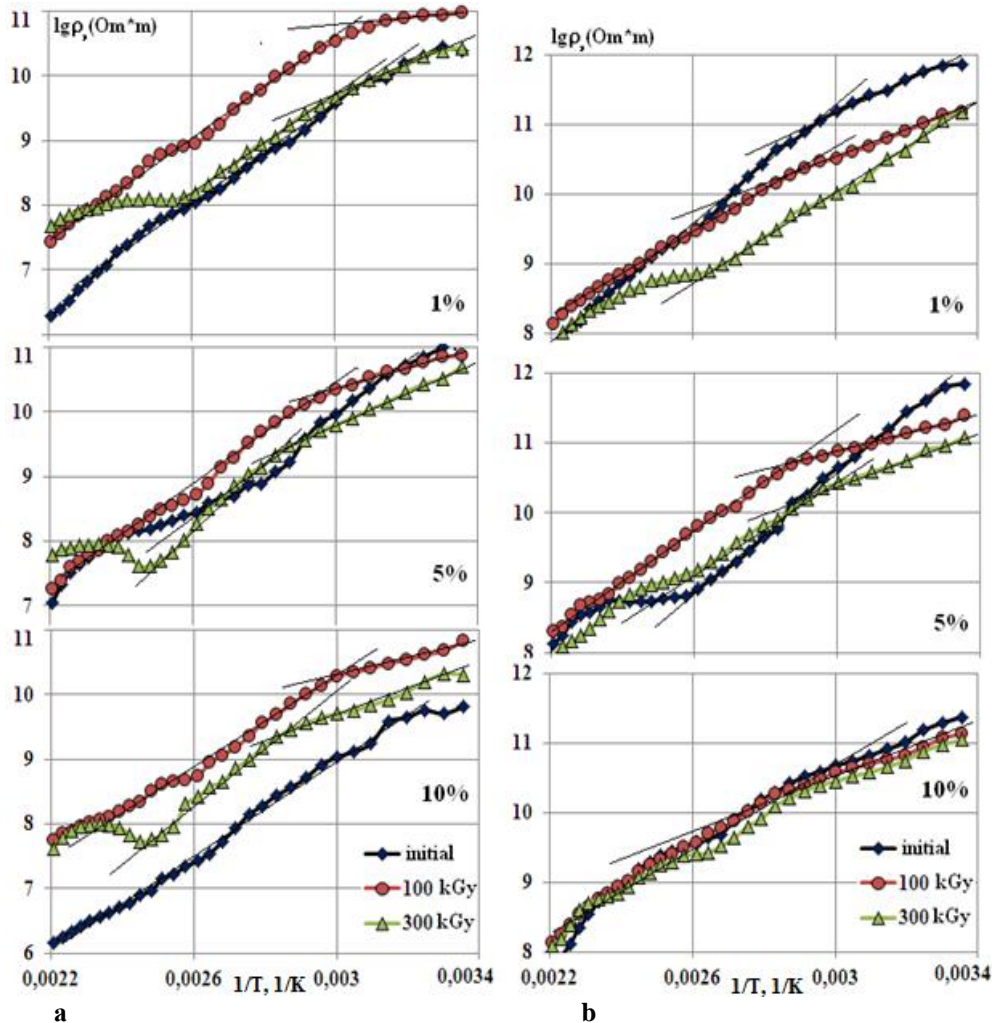


Fig.2. Temperature dependences of specific volume resistance of P(VDF-TFE) composites with micro-Si (a) and nano-Si (b) irradiated by different doses.

Table

The activation energy value of electric conduction of P(VDF-TFE) and P(VDF-TFE)/Si composites with micro- and nano-particles irradiated by different doses.

	Dose, KGy	Micro-Si		Nano-Si	
		$\Delta E_1$ , eV	$\Delta E_2$ , eV	$\Delta E_1$ , eV	$\Delta E_2$ , eV
100% P(VDF-TFE)	0	-	0,33	-	0,33
	100	-	0,298	-	0,298
	300	-	0,27	-	0,27
1%	0	-	0,36	0,2	0,387
	100	0,036	0,31	0,17	0,26
	300	0,15	0,324	-	0,258
5%	0	-	0,31	-	0,39
	100	0,13	0,33	0,1	0,31
	300	0,21	0,42	0,15	0,29
10%	0	-	0,32	0,18	0,25
	100	0,113	0,298	0,18	0,25
	300	0,165	0,36	0,18	0,25

We suppose that radicals and matrix oxidation appearing as a result of gamma radiation influence can lead to formation of oxygen bonds C-O-Si with filler surface in composite. Thus, the release of charges bound with surface of silicon particles becomes difficult in region below composite melting point because of relatively strong interaction and changes take place because of charges released from polymer matrix.

The some resistance stabilization region is observed only in samples irradiated by dose 300KGy in  $lg\rho = f(1/T)$  temperature dependences of P(VDF-TFE)/Si composites with silicon nano-particles (fig.2b). On the base of comparative analysis of these dependences one can say that radiation exposure up to dose 300KGy is accompanied by cross-linking in polymer matrix and increase of interphase layer interaction with oxidized active surface of nano-silicon filler in distinct from composites with micro-silicon filler. From temperature dependence of initial and irradiated composites with 10% silicon volume content it is seen that all three curves coincide with each other with some error. Using  $lg\rho_v = f(1/T)$  the activation energy values  $\Delta E$  corresponding to each inclination of rectilinear part of curves are calculated. The observable curve step and comparison of  $\Delta E$  activation energy values from table show that composites

with (10% volume content) nano-silicon are relatively stable to gamma irradiation exposure. The redistribution of radiation energy on volume takes place in P(VDF-TFE)/10%Si composites with nano-particles, energy part influencing on polymer matrix interface with nano-particles increases that leads to stable character of sample conductivity. Thus, at one and the same filler content the particle concentration in composites with nano-particles has the relatively high value. The transition from micro-particles to nano-particles is accompanied by increase of filler effective surface and concentrations of C-O-Si bonds with surface and this leads to mobility decrease and resistance increase that we experimentally observe. At introduction of micro-fillers the concentration of C-O-Si bonds becomes relatively low because of effective surface decrease, macro-molecule mobility increases and resistance decreases correspondingly that reflects on activation energy values [16]. In conclusion we can say that observable changes in electric properties of irradiated composites on P(VDF-TFE) base with micro- and nano-particles of silicon are connected by both processes of radical formation and oxidation with further cross-linking and destruction in heterogeneous system (polymer matrix and filler) and redistribution of absorbed radiation energy between components of composite.

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