Effective Changes In Polymer Nanocomposite Materials When They Are Modified With γ-Rays

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Abstract: Composite materials based on polymer fillers have been intensively studied in recent years, and in many cases, polymer nanocomposites find new applications in the preparation of certain sensors (recorders), surface coatings of spacecraft, especial type of the sensors. In addition, it is known that the change in the size of the fillers, the resistance of the composite materials to the influence of various types of radiation (γ -rays, electron, e-rays, ultraviolet rays, etc.), electrical conductivity, etc.), the study of which is still relevant today, and occupies a large place in radiation materials science. It can be noted that composite materials consisting of polymer - nanoscale fillers occupy a key place in many global research centers of the world. The purpose of the work is to obtain and study new electroactive (electret, antistatic, radiation-sensitive) polymer composite materials. Polypropylene was used as binder and Al_2O_3 oxide as filler in this work. In other research works, the sizes of the oxide fillers were large. In this study, nanofillers were used. Experiments show that as the size of oxide particles decreases, its electret properties improve. At the same time, the relaxation process of electret charges of polymer composites also depends on the value of the initial irradiation dose of γ-rays. As a result of studying the relaxation α-, β- and γ- processes of PP/α - Al_2O_3 composites in the temperature range of $100 \div 500$ K by the radio-thermo-luminescence (RTL) method, it was determined that the maximum at T = 230 K, the observed luminescence peak from the filler concentration (($20 \div 40$) % α - Al_2O_3) and varies proportionally depending on the radiation dose, and it can be used as a dosimeter in γ-dosimetry at a dose rate of up to 50 kGr.

Key words: high frequency rays, modification, RTL, relaxation, matrix, filler, electret, nano-filler, matrix, crown electrets

1 Introduction

Application of materials obtained as a result of modification of polymer composites with high-frequency rays in science and technology does not lose its relevance [1,2,3]. It is possible to control the electret properties of

composite materials not only by modification with radioactive rays, but also by different nano-fillers, as well as by changing the amount of fillers by volume % [4,5,6].

Using dosimetry was proposed for the first time by Fabel G. and Henich H. based on the laws of reduction of the effective density of electret charges σ_{ef} under the influence of radiation dose of polymer electrets [7]. It is proposed to express the dependence of the dose σ_{ef} in the range of 1 kGr ÷ 10 MGr by the formula $\sigma_D/\sigma_E = contlgD$. $\sigma_{ef} = f(D)$ dependences is differ for the different polymer electrets. In order to increase the sensitivity of electrets to γ-rays, the possibility of using electrets based on polymer nanocomposite materials modified by γ-rays was experimentally studied [8].

It is known that the dependence of the physical-mechanical and electro-physical properties of polypropylene (PP) films on the dose of γ-irradiation reaches the maximum value at the values of the dose D = 50÷100 kGr [9,10]. At the same time, the electret parameters of PP-based PP/SiO_2 composites take an extreme value $\left(\sigma_{ef} \sim 5 \cdot 10^{-5}\ Kl/m^2\right)$ at a certain amount of an aerosilin. As we mentioned above, relaxation of stabilized (electret charges) or unstable charges in oxide-based crown electrets is of great interest if we modify PP in advance with small dose values and PP/SiO_2 , PP/Al_2O_3, PP/Fe_3O_4, PP/Fe_2O_3, PP/TiO_2 etc., made of that polymer. The case of electret charge in composites based on PP/metal oxides has been studied [11]. The analysis of these materials shows that the surface density σ_{ef} of electret charges and its degree of stability depend nonlinearly on the amount of filler. The results of research conducted in these directions are of great interest. Thus, the simultaneous effect of various fillers and γ-rays on the structure of PP leads to interesting results.

2 Experiment

In the performed work, PP powder matrix was mixed with α - Al_2O_3 filler (filler sizes of α - Al_2O_3 - 10÷15 nm) together in a porcelain container. Then, composite samples with a thickness of 50÷100 μm and a diameter of 20÷40 mm were obtained from this mixture obtained in a hydraulic press at a pressure of 15 MPa at a temperature of 423÷443°K for 5 minutes. The received nanocomposite samples were irradiated at different doses in the MPX-ɣ-25M isotope device with a ^{60}Co radiation source.

Then, electro-physical parameters (ε, tanδ) of the synthesized nanocomposite samples, characteristics of α-, β- relaxation processes were studied based on the analysis of radio-thermo-luminescent RTL spectra with the TLQ-69M device. Based on the above considerations, the values of the proposed models for calculating the dielectric permeability of polymer nanocomposites are given in Table 1. The values of the dielectric permeability of the initial samples can be calculated using the following formulas [12]:

on Odelevsky
$$\varepsilon = \varepsilon_2 \left[1 + \frac{v_1}{(1-v_1)/3 + \varepsilon_2/(\varepsilon_1 - \varepsilon_2)} \right] \quad (1)$$
$$\varepsilon = \frac{\varepsilon_1 \cdot \varepsilon_2}{\gamma_1 \varepsilon_1 + \gamma_2 \varepsilon_2} \quad (2)$$
on Tareyev [19]
$$\varepsilon = \gamma_1 \varepsilon_1 + \gamma_2 \varepsilon_2 \quad (3)$$

The values of ε calculated on the basis of different models (1), (2) and (3) are given in table 1. If the dimensions (dispersion) of the filler are in the order of tens of nanometers, for this case phenomenology calculation formula for the dielectric permittivity of the nanocomposite ε_k is given in [13]

$$\varepsilon_k = \varepsilon_p \left[1 + \varphi \frac{(\varepsilon_p + 2)}{3} \cdot \frac{d_{max}^2}{3\varepsilon_0 V_0 kT} \right] \quad (4)$$

where d_{max}^2-the maximum value of the dipole moment; V_0 - the free volume around the

nanoparticle expressed by $V_0 = \frac{4}{3}\pi r^3$; k - Boltzmann's constant.

From the values of dielectric constants given in Table 1, it can be concluded that at low amounts of α-Al$_2$O$_3$ in PP - up to 10÷15 volume %, satisfaction with the experimental values of ε is observed. For higher amounts of α - Al_2O_3 in the composite, it is probably necessary to use other reporting formulas [14]. It should be noted that in the work done, by us [15] and other authors [14,16,17] have shown that depending on the amount, dispersion and nature of the filler, their modifying effects also depend on the crystallization conditions of the polymer.

Table 1

Calculated values of dielectric permittivity of two-component $PP/\alpha - Al_2O_3$, nanocomposite samples at a frequency of $6 \cdot 10^3$ Hz based on different models (1), (2) and (3)

α - Al_2O_3 amount in volume %	Formulas for calculating ε for filled polymers		
	(1)	(2)	(3)
15	8,92	9,25	2,50
20	8,4	8,84	2,61
30	7,45	8,01	2,88
40	6,51	7,18	3,22

T_g glass transition temperature (β-relaxation), which is an effective structural parameter characterizing molecular mobility, is well monitored by RTL and TSD (thermal stimulated depolarization) methods [15,18]. The RTL spectra of the initial samples irradiated with γ-rays in similar modes and those composite samples are given in figure 1. RTL curves for PP show maxima at 125, 190±2 (γ-process), 273°K (β-process) and 334±2 K (α-process), respectively. Peaks in the areas of realization of β- and α-processes have a relaxation nature, and when filler is introduced, their intensity and temperature states change significantly. When α - Al_2O_3 nano-filler is introduced into PP, α- and β-processes undergo a great change (the character of devitrification changes).

Figure 1. RTL spectra of the initial PP (a) , α - Al_2O_3 (b), $PP/\alpha - Al_2O_3$, (c) composite samples irradiated with γ-rays in similar modes:
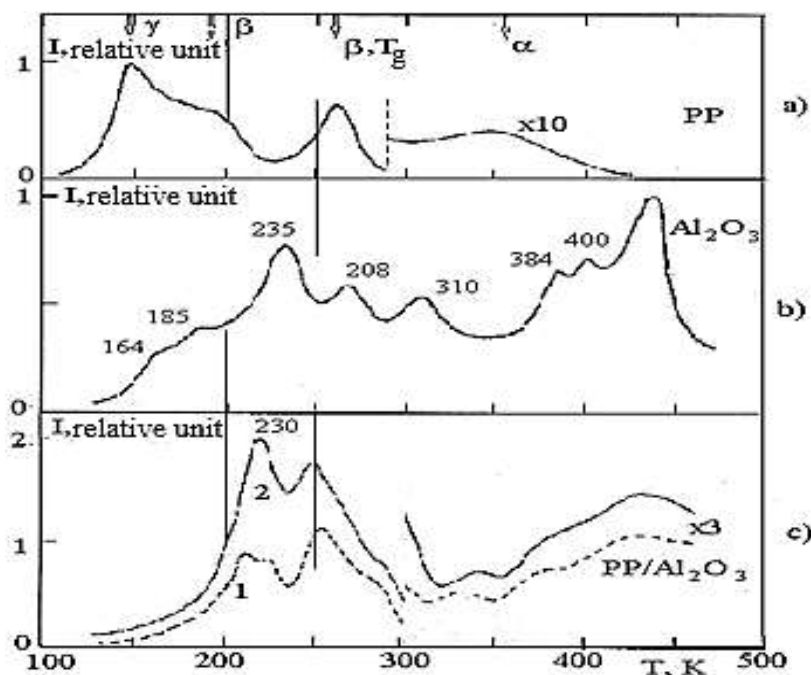
$1 - PP + 20\%\alpha - Al_2O_3; 2 - PP + 40\%\alpha - Al_2O_3$.

When $T > T_\alpha$, and the share of $\alpha - Al_2O_3$ in the composite increases, the peaks of high-temperature radiation increase in intensity and become very sensitive to the absorption dose of γ-radiation (at $T = 456\,К$). Characteristic RTL illumination spectra of $\alpha - Al_2O_3$ samples obtained in a similar irradiation mode are given in figure 1 (curve 2). Currently, there is no general idea about the nature of these peaks. As a result of conducted radio thermal luminescence (RTL) studies, it was determined that the RTL spectrum is characterized by luminescence peaks with centers corresponding to 164, 185, 235, 268, 310, 384, 400 and 460 K. According to the existing literature, low temperature peaks are related to low concentration additives, chemisorbed O_2 and OH groups. The peaks observed at 235 and 310 K, respectively, are due to the presence of O-shaped holes and autolocalized excitons (exciton-electron-hole pair). It is assumed that recombination processes take place in the structure of $\alpha - Al_2O_3$ during

the re-formed structures at these indicated temperatures. As can be seen from the radio thermal luminescence curve in point a) of Figure 1, the main dosimetrically peak has a complex structure and is asymmetric. In addition to the main peak, at a relatively low temperature, relatively medium-intensity luminescence peaks with maxima centered at 384 and 400 K are observed, which is due to the presence of some additives in the $\alpha - Al_2O_3$ samples. According to the analysis of the chemical composition, aluminum oxides contain ions of Cd, Co, Cr, Fe, Mg, Ti additives, and the amount of chromium ion is ~2,5·10⁻³ weight % [19]. Peaks at temperatures of 168, 310, (384÷400) K are related to Mg, Ti additions.

The dependences of the main dosimetric peak and its 4 characteristic parameters on radiation dose indicated in point b) of Figure 1 allow to use $\alpha - Al_2O_3$ as a thermal luminescent dosimetric. The radio thermal luminescence light curves of the composite samples obtained on the

basis of PP with different concentrations of $\alpha - Al_2O_3$ oxide fillers are shown in Figure 1 (c). Curve 1 shows $PP + 20\% \, \alpha - Al_2O_3$, curve 2 shows $PP + 40\% \, \alpha - Al_2O_3$. As can be seen from the figure, changes in the RTL curves occur as a result of the increase in the volume % of the oxide filler. In the area of the main dosimetric peak $(T = 350 \div 500 \, \text{K})$, the shape of the illumination curves deteriorates and has a spread shape.

However, the intensity of the radio thermal luminescence curves whose centers correspond to the temperature of 235 and 268 K increases and their centers shift slightly. This shift is probably the result of the interaction between PP and oxide. It should be noted that $PP + 20\%$ irradiated at different doses is the observed and relatively narrow maximum $(T_{max} = 230 \, K)$ in $\alpha - Al_2O_3 \alpha$ composites. The linear variation of the intensity of the radio thermal luminescence curve depending on the radiation dose (more precisely) suggests that it is possible to use the obtained composites as dosimeters. Thus, the newly obtained dosimetric peak is located in the temperature region 2 times lower than the main peak and differs from the main peak in the absence of additional peaks.

The radiation peak observed in the RTL spectrum at temperature $T = 456 \, K$ increased linearly with the amount of Al_2O_3, indicating that interfacial phenomena affect most properties of polymer composites. Therefore, in already formed polymer composites and composites based on nanoscale fillers, this phenomenon is given wide attention, and new hypotheses and models are proposed [20]. If the interphase structure (FAS) is not formed between the filler and the polymer matrix, then the macro properties of the composite deteriorate [21]. The interaction between the fillers with different dispersion and the polymer matrix leads to nano-adhesion, fractal, etc. so-called structural units are included [21,22]. The modification process is usually divided into three types - physical, chemical and structural.

3 Result

As a result of studying the relaxation α -, β - and γ - processes of PP/α - Al_2O_3 composites in the temperature range of $100 \div 500 \, K$ by the radio-thermo-luminescence (RTL) method, it was determined that the maximum at $T = 230 \, K$, the observed luminescence peak from the filler concentration $((20 \div 40)\% \, \alpha - Al_2O_3$ and varies proportionally depending on the radiation dose, and it can be used as a dosimeter in γ-dosimetry at a dose rate of up to 50 kGr. It is shown that the intensity of the radiation peak observed in the RTL spectrum at temperature T=456 K increases linearly with the amount of Al_2O_3, which is explained by our proposed three-phase supramolecular structure model of crystallized polymers.

In this work, it was clarified that the sensitivity to radiation depends on both the amount of $\alpha - Al_2O_3$ filler and the dose of radiation. It was found that by changing the percentage of fillers and the radiation dose, it is possible to change the physical properties of these composite materials and control their electrolytic properties.

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The authors equally contributed in the present research, at all stages from the formulation of the problem to the final findings and solution.

Conflict of Interest
The authors have no conflicts of interest to declare that are relevant to the content of this article.