

INFLUENCE OF GAMMA RADIATION ON ELECTROPHYSICAL PROPERTIES OF NANOCOMPOSITES OBTAINED ON THE BASIS OF HIGH-DENSITY POLYETHYLENE AND NANO-SIZE SiO₂

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Abstract: Herein, the results of the study of the effect of ionizing γ -radiation on the electro-physical properties of HDPE/SiO₂ nanocomposites obtained at different volume ratios have been presented. It has been shown that the changes in the molecular structure of the polymer due to the influence of γ -radiation on the HDPE/SiO₂ nanocomposites have a significant effect on the dielectric properties and relaxation processes of the material. The electro-physical properties of the composites are determined by the relaxation processes of accumulated charge on the inter-phase boundary of polymer-filler and crystallite-amorphous phase in the polymer matrix and these properties can be controlled by the influence of gamma radiation

Keywords: high-density polyethylene (HDPE), silicon dioxide (SiO₂), nanocomposite, interphase layer, dielectric spectroscopy, relaxation, gamma radiation

1. Introduction

Inorganic fillers and polymer-based composite systems are the most relevant and important group of materials in terms of their large-scale application and irreplaceable hybrid properties. For this reason, the synthesis and development of polymer-based nanocomposite materials in various areas of science, technology and industry is one of the main priorities. Thus, the acquisition of two-component hybrid systems by adding nano-SiO₂ filler to polymer matrix provides endless practical opportunities in modern micro and nanoelectronics, as well as in highly sensitive sensor technology and functional smart materials industry. The properties of materials obtained by the addition of nanosize fillers to the polymer matrix show superior properties as a result of synergistic effects, that is, the combined properties of the polymer and the filler are higher than those shown separately. Of course, it is worth noting the change in the properties by the sharp increase of the interphase layer with the insertion of the filler into the polymer matrix. A large number of authors have shown that this effect can be observed even at very low concentrations of fillers [1-4]. For example, the following authors have shown that although permittivity of inorganic fillers such as Al₂O₃, MgO, SiO₂ and BN are close to the polymer matrix, the permittivity of nanocomposites obtained by their inclusion into the polymer matrix can significantly increase in very small volume fractions of nanoparticles [5].

Despite the above, the main purpose of our present work was to investigate the influence of γ -radiation on the electro-physical properties of HDPE/SiO₂ nanocomposites obtained at different volume ratios.

1. 2. Sampling and measurement techniques

High-density polyethylene (HDPE) of 20806-024 brand with a molecule mass of $95 \cdot 10^3 \text{ g/mol}$, crystallinity degree - 60%, melting temperature - 130°C , density - 958 g/cm^3 was used as polymer matrix during the acquisition of nanocomposites. And, $\alpha\text{-SiO}_2$ (Sky Spring Nanomaterials, Inc. Houston, USA) nanoparticles with a special surface area of $S=160 \text{ m}^2/\text{g}$, density - 2.65 g/cm^3 , particle size - 20-30 nm, purity degree - 99.9%, having an amorphous structure with spherical morphology was used as a filler.

The composite samples were prepared by thermal pressing of homogeneous mixture of components taken at different (1, 3, 5, 10, 20%) volume ratios, at 438K, under 15 MPa pressure, for 10 minutes, and then instantaneous cooling it in a water-ice system. The electro-physical parameters of the obtained "sandwich" type samples were measured using an E7-20 immitansmeter. Samples were irradiated at room temperature ($T=298\text{K}$), in MPX- γ -25M type γ -radiation device with ^{60}Co radiation source [6, 7].

2. Results and discussions

Frequency dependences of real $\varepsilon'(\nu)$ and imaginary $\varepsilon''(\nu)$ parts of complex value $\varepsilon^*(\nu)$ of permittivity of HDPE/SiO₂ composite samples, initial and irradiated at different doses (100, 300 kGy) by γ -radiation, defined at a room temperature have been given in Figure 1. It should be noted that the real and imaginary parts of the permittivity were calculated using the following equations:

$$\varepsilon' = \frac{C_p \cdot d}{\varepsilon_0 \cdot S} \quad (1)$$

$$\varepsilon'' = \varepsilon' \cdot \text{tg} \delta \quad (2)$$

Here, C_p is electrical capacity of the sample, d – the thickness of the sample, S - electrode surface area, ε_0 – dielectric constant of vacuum ($\varepsilon_0 = 8,85 \cdot 10^{-12} \text{ F/m}$), $\text{tg} \delta$ - tangent of dielectric loss angle.

As can be seen from the figure, the values of the real and imaginary parts of the permittivity are high in low-frequency regions (100Hz – 1 kHz) both before and after irradiation, but in the high-frequency regions, it sharply decreases starting from 5 kHz and then it remains completely stable. This law has been proven by sufficient scientific evidence that has already been explained in research. Thus, the tendency to the decrease of permittivity with increasing frequency in different dielectrics, especially polymer-based composite materials, is explained by various polarization mechanisms and relaxation effects [8, 9]. It should be noted that the real value (ε') of the permittivity is a measure of the polarization amount of the material in a physical sense, and describes the ability of the material to collect the energy of the electric field, that is, the electrical capacity. However, the imaginary value (ε'') of permittivity describes the part of electric field energy, accumulated in the material, which is converted into thermal energy, that is, lost energy. As it is seen, the values of real part of the permittivity of nanocomposites increases sharply in the low-frequency region (100 Hz - 1 kHz) compared to pure polymer, both before and after irradiation depending on volume of filler. This increase can be seen even in the lowest filler volume (1%). Naturally, this increase is due to the polarization in the interphase boundary between the polymer matrix and the filler under the influence of the external electric

field, more precisely due to the Maxwell - Wagner - Sillars effect. Usually this polarization occurs between interphase macroscopic surfaces with different conductivity and having permittivity, of two or more phase heterogeneous systems. It should be noted that interfacial polarization is characterized by a higher relaxation period than other polarization types. As the dependencies show, while the real and imaginary part of the permittivity decreases at 100kGy in comparison with the corresponding parameters of the initial samples, the increase in these parameters at the dose 300kGy starts again.

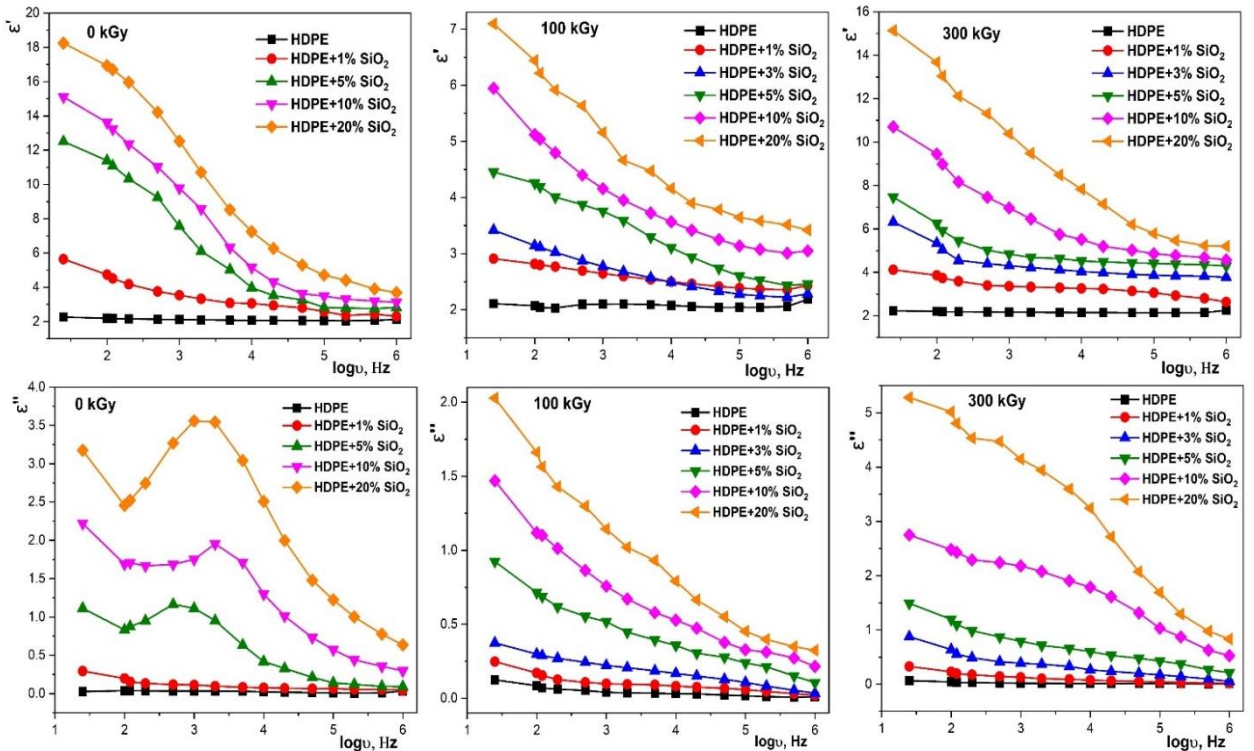


Fig. 1. Frequency dependence of real $\epsilon' = f(\nu)$ and imaginary $\epsilon'' = f(\nu)$ parts of the permittivity of polymer nanocomposites $HDPE+\%SiO_2$ with different volume fraction before and after irradiation

We consider that this is due to the increase of the radiation construction process in polymer matrix and between the matrix and nanoparticle surface around the 100kGy dose, and of the destruction process in the matrix and interphase boundary when approaching 300kGy dose. It is seen that all these factors cause the peaks, characterizing the relaxation process from 5% volume amount of filler, to shift to high-frequencies in the frequency dependence of dielectric losses of polymer nanocomposite $HDPE/SiO_2$ and to increase their half-width (Figure 2). It is known that the relaxation period is determined by the time it takes to transfer the relaxators that make up the dielectric, i.e. molecules, from the excited state to the stable. The polarization process occurs more conveniently when the electric field frequency is lower than the relaxation frequency. At this time, the dielectric losses in the material are very low. If the frequency of the external electric field increases and becomes equal to the relaxation frequency, then we observe the resonance state of dielectric parameters, that is, the maximum value. The subsequent increase in the frequency of the external electric field weakens the polarization process and the parameter values begin to decrease. The dielectric losses depend on the type of polarization and dielectric losses occurring in about 10^{-3} - 10^4 Hz frequency region characterize the inter-phase Maxwell – Wagner polarization. Dielectric losses during dipole polarization are observed at a frequency of

10^8 Hz, losses due to atomic polarization are at 10^{12} Hz, and dielectric losses due to the electron polarization are observed at 10^{16} Hz [10].

Along with all this, the increase in permittivity due to inter-phase polarization sometimes impedes the material's ability to accumulate energy. Thus, the local electric field generated by the charges accumulated in the interphase layer gets very high value, which results in a decrease in the alternating current (AC) conductivity and the electrical strength of the material and in an increase in dielectric losses [10].

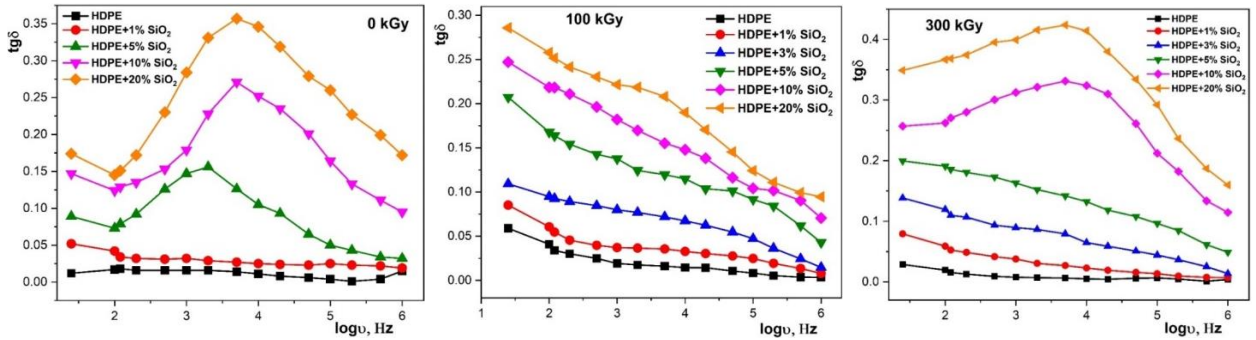


Fig. 2. Frequency dispersion of $tg\delta = f(\nu)$ of dielectric loss angle tangent in HDPE+% SiO₂ polymer nanocomposites before and after irradiation

Along with this, the dependence of the permittivity (ϵ) and dielectric loss angle tangent ($tg\delta$) of the HDPE/SiO₂ nanocomposites initial and irradiated by gamma-radiation at different doses, which were defined at a constant frequency, on the volume amount of filler (Figure 3). It was found that the samples' permittivity and dielectric loss angle tangent increase by exponential law in all doses depending on the volume amount of the filler. However, the permittivity of the sample under a dose of 100 kGy is lower than that of the sample under 300 kGy dose. We believe that the increasing number of constructions in the composite structure, matrix and polymer-filler interphase boundary layer at a dose of 100 kGy decreases the polarization capability by reducing the relaxors (polymer chains) mobility, increases the activation energy of the associated charges and as a result, the permittivity of the sample decreases. Increasing the absorbed dose up to 300 kGy results in a relative increase in permittivity due to the small-sized aggregates formed due to the destruction processes in the composite structure and increased polarization ability of free elements of the chain.

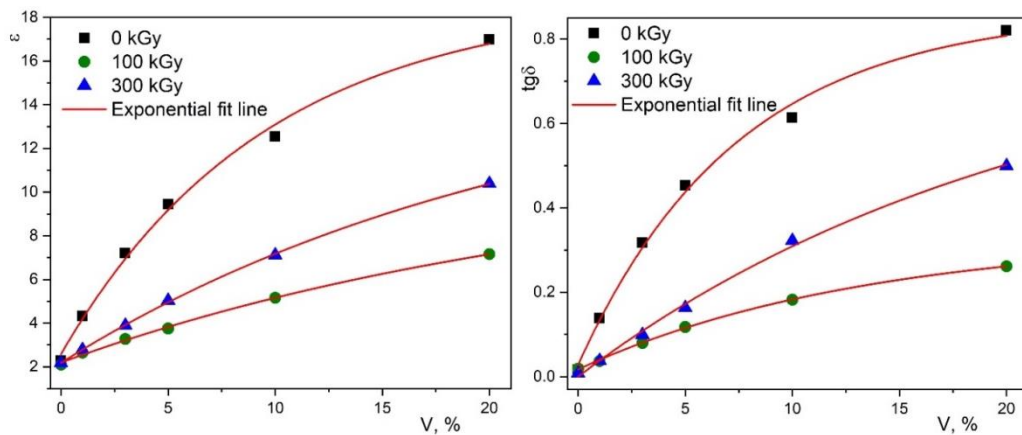


Fig. 3. Dependence of permittivity (ϵ) and dielectric loss angle tangents ($tg\delta$) of YSPE/SiO₂ nanocomposites initial and irradiated by gamma radiation at different doses on the volume amount of filler at constant frequency ($\nu = 1$ kHz)

The formation of a special interaction zone, that is, the third phase between nanoparticles and polymer chains in the composite materials obtained when nano-size filler was added to the matrix is nothing new and has been mentioned by many authors [9, 11, 12]. The amount of the third phase (effective surface area) formed between the particles and polymer matrix sharply increases when the filler size is lower than 100 nm, and it plays a very important role in modifying the physical properties of the material. It is known that the interphase area in nanocomposites sharply depends on the activity, form and geometric parameters of nanoparticle surface. Therefore, the interphase area can be regarded as a layer with a certain thickness formed between polymer matrix and particle. Sometimes, polymer nanocomposites containing spherical morphology fillers are presented as 0-3 systems with a certain thickness and volume [13].

In order to identify the influence of thermal activation on the dielectric relaxation processes of irradiated polymer nanocomposites HDPE/Si₂, we investigated the temperature dependences of dielectric permittivity (ϵ) and dielectric loss angle tangent ($tg\delta$) (Fig. 4)

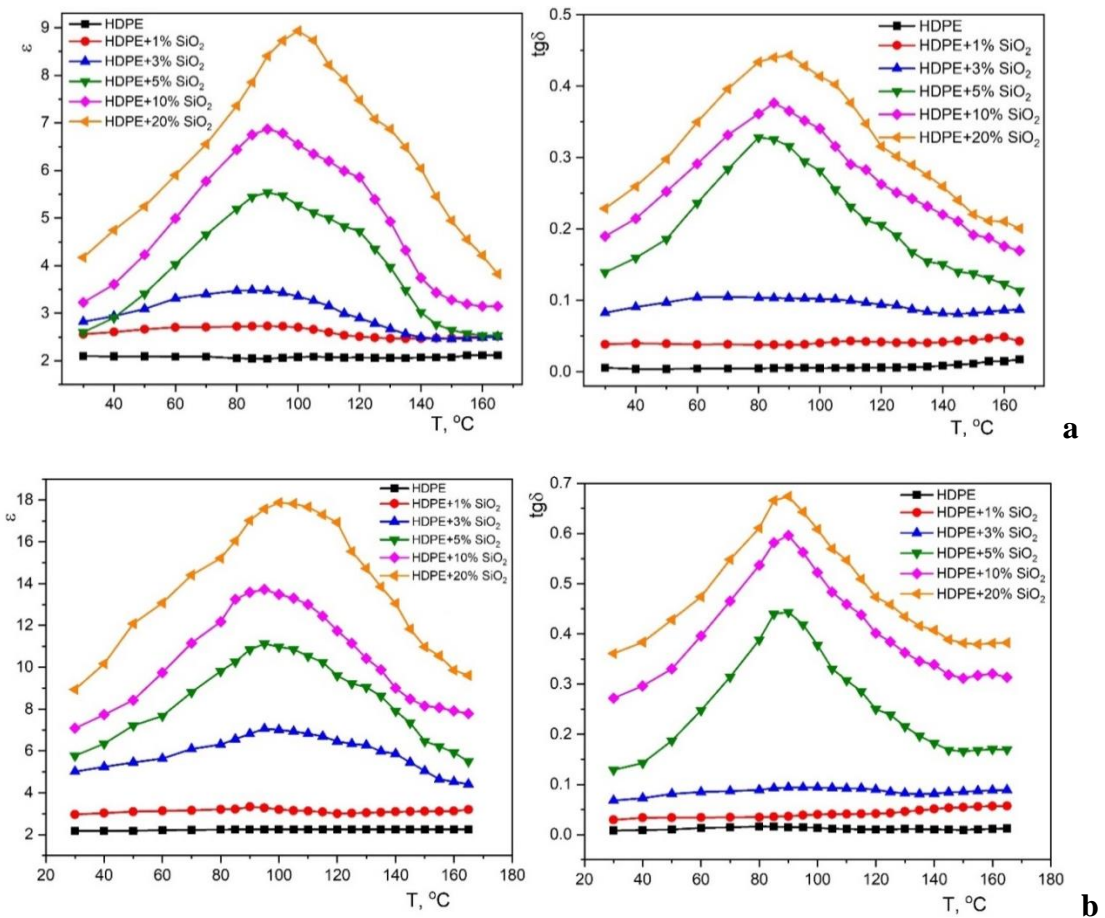


Fig. 4. Temperature dependence of permittivity (ϵ) and dielectric losses ($tg\delta$) of HDPE/SiO₂ polymer nanocomposites irradiated at different doses: a-100 kGy; b-300 kGy

As it is seen, in the polymer matrix, two relaxation peaks are observed at the temperature ranges of 70-110°C and 110-140°C in the values of both dielectric permittivity and dielectric loss angle tangent starting from 3% volume fraction of filler. We believe that the relaxation peaks observed at 70-100°C temperature range occurs due to the melting of crystallites in the polymer matrix by the influence of temperature and to the thermal degradation of crystal-amorphous interphase boundary. But, the relaxation peaks formed in the high temperature regions (100-

130°C) occurs due to the thermal relaxation of charges of Maxwell-Wagner polarization in polymer-SiO₂ interphase layer [14-15]. On the other hand, as we mentioned before, while dielectric permittivity and loss of the sample irradiated at 100kGy dose decrease due to the influence of construction and destruction processes occurring under the influence of ionizing radiation, these parameters sharply increase in the samples irradiated at 300kGy dose. The decrease in the half width of the peak in the $tg\delta = f(T)$ dependence of these samples and its shift to the low temperatures give us reason to say that the destruction process mainly affects the crystalline and amorphous phases of the polymer. Thus, we can say that relaxation processes observed during the temperature dispersion of dielectric permittivity $\varepsilon = f(T)$ and dielectric loss angle tangent $tg\delta = f(T)$ in the polymer nanocomposites HDPE/SiO₂ confirm the results we obtained during TSD measurements [14]. As the electro-physical properties of these composites are defined by the relaxation processes of charges accumulated in the crystallite-amorphous and polymer-filler interphase boundary in the polymer matrix, it is possible to control these properties by the influence of gamma influence.

3. Conclusion

The changes, occurring in the molecular structure of the polymer due to the γ -radiation influence on the dielectric properties of nanocomposites HDPE/SiO₂ obtained by the addition of inorganic nano-SiO₂ filler with different volume amount to the polymer matrix and on the relaxation processes, have a significant effect on the electro-physical properties of the material. As the electro-physical properties of these composites are defined by the relaxation processes of charges accumulated in the crystallite-amorphous and polymer-filler interphase boundary in the polymer matrix, it is possible to modify these properties by the influence of gamma influence.

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ВЛИЯНИЕ ГАММА ИЗЛУЧЕНИЯ НА ЭЛЕКТРОФИЗИЧЕСКИЕ СВОЙСТВА НАНОКОМПОЗИТОВ ПОЛУЧЕННЫХ НА ОСНОВЕ ПОЛИЭТИЛЕНА ВЫСОКОЙ ПЛОТНОСТИ С НАНОЧАСТИЦАМИ SiO₂

А.А. Набиев

Резюме: В работе представлены результаты влияния гамма излучения на электрофизические свойства нанокompозитов ПЭВП/SiO₂ полученных при различном содержании наполнителя. Показано, что происходящие изменения в молекулярной структуре полимера после воздействия гамма излучения на нанокompозиты ПЭВП/SiO₂ достаточно сильно влияет на диэлектрические свойства и релаксационные процессы материала. Электрофизические свойства композитов определяется релаксационными процессами накопленного заряда в межфазной границе кристаллит-аморфная фаза в полимерной матрице и наполнитель-полимер в композите. Кроме этого имеется возможность управлять электрофизическими свойствами композитов воздействием гамма излучения.

Ключевые слова: Полиэтилен высокой плотности (ПЭВП), кремний диоксид (SiO₂), нанокompозит, межфазный слой, диэлектрическая спектроскопия, релаксация, гамма радиация

YÜKSƏK SİXLİQLİ POLİETİLENLƏ NANOÖLÇÜLÜ SiO₂ ƏSASINDA ALINMIŞ NANOKOMPOZİTLƏRİN ELEKTROFİZİKİ XASSƏLƏRİNƏ QAMMA RADİASİYANIN TƏSİRİ

A.A. Nəbiyev

Xülasə: İşdə müxtəlif həcm nisbətində alınmış YSPE/SiO₂ nanokompozitlərinin elektrofiziki xassələrinə ionlaşdırıcı γ -şüalanmanın təsirinin tədqiqinin nəticələri təqdim olunub. Göstərilmişdir ki, alınmış YSPE/SiO₂ nanokompozitlərinə γ -şüalanmanın təsiri nəticəsində polimerin molekulyar strukturunda baş

verən dəyişikliklər materialın dielektrik xassələrinə və relaksasiya proseslərinə ciddi təsir göstərir. Kompozitlərin elektrofiziki xassələrini polimer matrisada kristallit-amorf faza ilə polimer-doldurucu fazalararası sərhəddində yığılan yüklərin relaksasiya prosesləri müəyyənləşdirir və qamma şüalanmanın təsiri ilə bu xassələri idarə etmək olar.

Açar sözlər: yüksək sıxlıqlı polietilen (YSPE), silisium dioksid (SiO_2), nanokompozit, fazalararası təbəqə, dielektrik spektroskopiyası, relaksasiya, qamma radiasiya