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The effect of gamma irradiation on the dielectric properties of polyethylene-based composites with the CdS-ZnS quasibinary system

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Polyethylene-based composites with the CdS-ZnS quasibinary system were obtained with a component ratio of 10% CdS-ZnS; 30% CdS-ZnS; 50% CdS-ZnS. The temperature dependences of the dielectric constant (ε) and the tangent of the dielectric loss angle (tgδ) of samples of HDPE+CdS-ZnS composites irradiated with a dose of 100 kGy, 50 kGy, and 200 kGy were shown. The dependences of the dielectric constant and the tangent of the dielectric loss angle of HDPE+CdS-ZnS composites on the gamma-irradiation dose have been determined.

Keywords: gamma irradiation, polyethylene, dielectric constant, dielectric loss angle, composite.

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Introduction

Polymer composite materials (PCMs) are successfully used as emergency containment of nuclear reactor, in the power supply system of artificial satellites and spacecraft, where nuclear radiation is always present. Radiation-induced behavior of PCMs properties is an important aspect that should be paid special attention to when developing new PCMs operating under conditions of nuclear radiation. Therefore, new PCMs should have high radiation resistance and minimal dependence of properties on changes in environmental parameters. It should be noted that in the recent creation of new PCMs technology by radiation modification of polymers with additives of different nature, the prediction of physical-mechanical, in particular, strength properties of PCMs is connected with the consideration of structural features of polymer structure. The influence of gamma irradiation and filler concentration leads to phase transformation of the supramolecular structure (SMS) of the polymer matrix and, accordingly, on the properties of PCMs. Polymers and polymer composites modified with γ-rays, high-energy electrons, UV and other ionizing rays are accompanied by the formation of free radicals and excited states and this is the cause of physicochemical changes observed in the primary processes. After these factors, secondary radiation processes occur [1-5]. These include recombination, substitution reaction and post-radiation effects. These processes are reversible and cause structural changes (physical and chemical) in the irradiated polymer. The main characteristic of irradiation effects on polymers are structural changes (cross-linking, degradation, oxidation, and other chemical reactions), while the charge state changes due to the dielectric effect. Cross-linking-creation of intermolecular (cross-linking) bonds, destruction, breaking of bonds in the main chain and side groups, change of unsaturation, disappearance and formation of different types of double bonds C=C, cyclization, formation of intramolecular bonds, radiation oxidation reactions, chemical changes caused by radiation in polymers. Physical changes can be associated with changes in crystallinity and physical and mechanical characteristics of the polymer composite. It is important to note that the degree of change in certain characteristics of the polymer is determined by its physical state before irradiation, conditions of types, irradiation rate and dose. It should be noted that the effect of ionizing radiation on polymeric materials is accompanied by various radiation-chemical processes, proceeding, as a rule, by free-radical

mechanism. Along with the processes of ionization and excitation of medium atoms in the irradiated system there is an accumulation of volumetric charges that excite the electric field even in the absence of external applied voltage [6-9].

I. Experimental technique

The samples for the study were obtained by hot pressing a mixture of polymer and filler powders in a hydraulic press with heaters. Two poissons with heaters and smooth polished surfaces were fixed on the lower and upper nozzle of the press.

The methodology of obtaining at manufacturing of composite samples, both initial PE and PP, and composites on its basis, consisted in the following:

- mixing mechanically powdered phosphor additives with PE powder in a porcelain mortar until a homogeneous mixture was obtained;
- the mixture between two Al foils and a spacer with a thickness of 100 microns was kept for some time at the melting point of the polymer under a small pressure (1MPa);
- at the same temperature the pressure is slowly raised to 10^{-15}MPa, at which the sample is kept for 5 minutes, then the pressure is removed and the sample is quickly cooled in a mixture of water and ice;
- the dimensions of the samples were: thickness in the order of 100-120 microns, the diameter of the obtained samples was 45 mm;
- in order to ensure reliable electrical contact during the study of electrophysical properties on both working surfaces of composite samples electrodes from thin aluminum foil with thickness of 7 microns were pressed [10].

For radiation studies the sources of γ-radiation sources of ^{60}Co isotope, available at the Institute of Radiation Problems of Ministry Science and Education of Azerbaijan. The main gamma-sources were isotope units of K-25 or MRX-γ-25M type based on ^{60}Co with half-life of 5.3 years and activity of emitter 5×10^4 Curie at 293 K.

The discussion of the results

Figure 1 shows the temperature dependence of dielectric constant (ε) and dielectric loss (tgδ) of

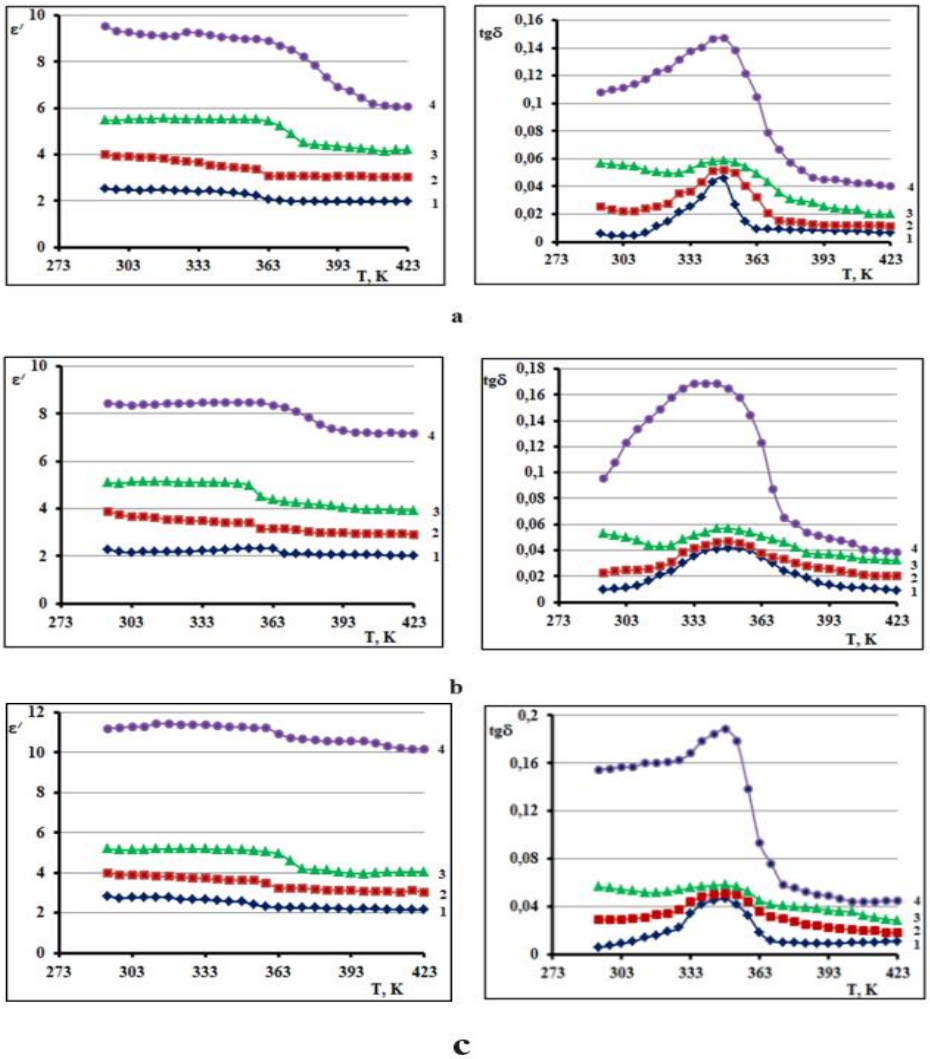

Fig.1. The temperature dependence of the dielectric constant (ε) and the tangent of the dielectric loss angle (tgδ) of samples of HDPE+CdS-ZnS composites irradiated with a dose of D = 100 kGy (a), D = 150 kGy (b), D = 200 kGy (c): 1- HDPE; 2-10% CdS-ZnS; 3-30% CdS-ZnS; 4-50% CdS-ZnS.

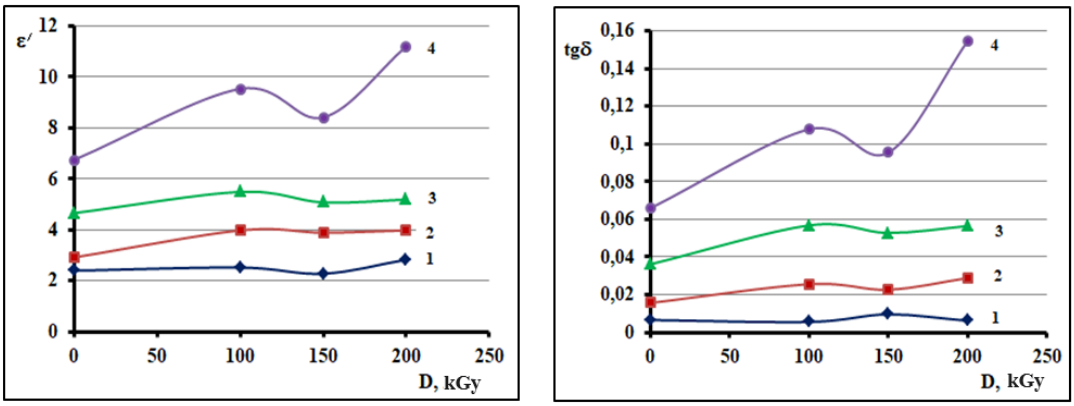

Fig. 2. Dependences of dielectric constant and dielectric loss of HDPE+CdS-ZnS composites on γ-irradiation dose: 1- HDPE; 2- 10%CdS/ZnS; 3- 30%CdS/ZnS; 4- 50%CdS/ZnS.

HDPE+CdS-ZnS composite samples irradiated with dose D = 100 kGy (a), D = 150 kGy (b), D = 200 kGy (c), respectively. Let us compare the unirradiated (initial) and irradiated samples: at 293 K, the dielectric constant values of unirradiated (initial) samples ε'=2.4 (pure HDPE), 2.92 (10%), 4.66 (30%), 6.75 (50%) (Fig.1 curves 1, 2, 3, 4). In irradiated samples, ε'=2.52 (pure HDPE, D=100 kGy), 2.98 (10%, D=100 kGy), 5.49 (30%, D=100 kGy), 9.54 (50%, D=100 kGy) (Fig.1.a), ε'=2.28 (pure HDPE, D=150 kGy), 3.89 (10%, D=150 kGy), 5.08 (30%, D=150 kGy), 8.42 (50%, D=150 kGy) (Fig.1.b), ε'=2.83(pure HDPE, D=200 kGy), 3.98 (10%, D=200 kGy), 5.19 (30%, D=200 kGy), 11.21 (50%, D=200 kGy) (Fig.1.c). It can be seen that the dielectric constant of unirradiated (initial) samples increases depending on the filler volume fraction (increases by 2.4-6.75, 2.8 times), and also the irradiated samples show an increase in the value of ε' (2.52-11.21, 4.45 times increase) depending on the absorbed radiation dose. A small change in the temperature dependence of dielectric permittivity of the polymer and composites with CdS-ZnS filler content up to 30% volumetric is observed with increasing irradiation dose. A relatively large change in the temperature dependence of dielectric permittivity is observed in HDPE+50%(CdS-ZnS) composites. We believe that this is the result of high filler content in the composite and interfacial Maxwell-Wagner polarization.

The temperature dependences of dielectric loss of irradiated composite samples (Fig. 1) show that the sample with the filler volume fraction F = 50% has the maximum value of tgδ=0.0314. The maximum value of dielectric loss tgδ can be related to both the filler content and molecular mobility of polymer chains, and the nature of the filler. It can be seen that relatively stable, initial values of dielectric loss of composites at doses of 100 and 150 kGy (tgδ=0.1) with increasing dose up to 200 kGy increases (tgδ=0.16). We believe that this is promoted by the increase in the concentration of volume charges at increasing irradiation dose, resulting in an increase in electrical conductivity and, accordingly, dielectric loss values of the composite system HDPE+CdS-ZnS.

Thus, at low filler contents (10 and 30%), due to the relatively perfect structure of the composites, the intensity of these maxima is low, but with an increase in the filler content to 50% by volume, the resulting loose structure of CdS-ZnS particles formed mainly from agglomerates leads to an increase in absorbed moisture and, accordingly, the intensity of these maxima increases.

As can be seen, the effect of radiation leads to a significant increase in the dielectric losses of the polymer and composites based on them. A significant increase in tgδ HDPE+CdS-ZnS composites in the temperature range of 293-348K may be due to radiation oxidation processes. This fact suggests that the reason for the increase in tgδ after storage may be the post-radiation-chemical oxidation of the polymer and polymer composite materials (PCMs). It should be noted that a slight increase in tgδ of irradiated HDPE and PCMs samples after storage at 293K is due to the gradual oxidation of primary alkyl radicals to peroxide radicals. Apparently, over storage time, radicals migrate from the crystal phase to the surface, where various polar oxygen-containing groups create more oxygen access and, thereby, lead to a change in the tgδ value.

Figure 2 shows the dependence of the dielectric constant (a) and dielectric losses (b) of HDPE+CdS-ZnS composites on the gamma-irradiation dose. The dependences show that changes in the dielectric constant and dielectric losses of composites on the radiation dose are similar. We believe that this dependence and tgδ on the absorption dose is the result of cross-linking, destruction and oxidation processes that occur when exposed to gamma radiation with HDPE+CdS-ZnS composites.

Conclusions

Thus, at relatively low radiation doses (up to 150 kGy), the prevailing cross-linking process, limiting the mobility of the molecular chain of the polymer matrix, leads to the stabilization of the measured parameters.

With a further increase in the radiation dose, a transition to destruction occurs, which is accompanied by the appearance of active centers and low molecular weight polar groups, as a result, an increase in the ε' and tgδ composites of HDPE+CdS-ZnS is again observed. With increasing absorbed dose, the degree of crystallization of the composite decreases, the crystalline structure gradually disintegrates and completely disappears at high

doses. Along with this change in the properties of the polymer matrix and on its basis composites is the process of disordered crystalline structure, as well as an increase in the number of dipole elements, which leads to an increase in ε' and tgδ.

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Вплив гамма-опромінення на діелектричні властивості композитів на основі поліетилену з бінарною системою CdS-ZnS

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Отримано композити на основі поліетилену з бінарною системою CdS-ZnS із співвідношенням компонентів 10 % CdS-ZnS; 30% CdS-ZnS; 50% CdS-ZnS. Показано температурні залежності діелектричної проникності (ε) і тангенса кута діелектричних втрат (tgδ) зразків композитів HDPE+CdS-ZnS, опромінених дозою 100 кГр, 50 кГр і 200 кГр. Визначено залежності діелектричної проникності та тангенса кута діелектричних втрат композитів HDPE+CdS-ZnS від дози гамма-опромінення.

Ключові слова: гамма-опромінення, поліетилен, діелектрична проникність, кут діелектричних втрат, композит.