

RADIOTHERMOLUMINESCENCE OF POLYETHYLENE POLYMER COMPOSITES WITH THE CdS/ZnS BINARY SYSTEM

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Polyethylene polymer composites with the CdS/ZnS binary system with different filler content were studied by radiothermoluminescence. It was shown that the introduction of a semiconductor additive (CdS/ZnS) into HDPE leads to a change in the intensity and temperature of the maxima on the RTL curves of the composite, which can be used to predict and evaluate the luminescent, dielectric, physical and mechanical properties of composites based on them.

Keywords: gamma-irradiation, polymer, polyethylene, radiothermoluminescence, CdS/ZnS.

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INTRODUCTION

The study of the processes of radiation modification of polymer materials and products is of interest to the electronic, cable and electromechanical industries. These materials have certain requirements, such as radiation and heat resistance, low dielectric losses, etc. [1,2]. Radiation exposure does not always lead to a deterioration in some properties of polymeric materials. Radiation-cross-linked polyolefins have been used in cable technology [3]. No less important are the issues of radiation modification of composite materials based on polymers dispersed with various fillers [4]. The study of the features of charge stabilization, interfacial and polarization phenomena in these composite materials is also relevant when predicting their performance properties. It should be noted that the effectiveness of the effect of fine fillers of these metal oxides on polypropylene (PP) or other polyolefins also significantly depends on the crystallization conditions and the method of producing (extrusion, pressing) the composite. Compositions obtained under deep melt hardening at $T = 273\text{K}$ have a more uniform structure and are easy to process, and also have high mechanical and electrical strength [5,6]. Equally important is the task of predicting the degree of radiation change in the structure and properties of polymers. For this purpose, the radiothermoluminescence (RTL) method is widely used [7,8]. The degree of effect of electrons and gamma irradiation on the polymer structure is judged from the RTL illumination curves and the position of the β -maximum (the onset of vitrification temperatures) in filled polymers.

This article presents the results of studies of polyethylene polymer composites with the CdS/ZnS binary system by radiothermoluminescence.

METHODOLOGY OF EXPERIMENTS

Samples of composites in the form of films $200 \pm 10 \mu\text{m}$ thick were obtained by hot pressing (at a pressure of 15 MPa for 5 minutes and at a temperature 10-200 above the T of the polymer matrix) of premixed powders of polymer and filler. The filler content in the composite was up to 10-15 vol.%. The fillers were powders with sizes $1 < d \leq 10$ microns of binary

compound CdS/ZnS. These technical ceramics are radiation-resistant. Thermoluminescence studies were carried out on a TLG-69M apparatus. The samples were irradiated at 77 K in pre-vacuumed at $1.3 \cdot 10^{-3}$ Pa ampoules with a Co^{60} γ -radiation source on the RHM- γ -25 unit up to 10 kGy.

RESULTS AND THEIR DISCUSSION

The radiothermoluminescence (RTL) method is based on the observation of thermoluminescence of investigated substances irradiated at low temperatures by fast electrons or gamma rays. Such luminescence (radiothermoluminescence) is associated with the recombination of charged particles stabilized in the substance during its irradiation. A characteristic feature of radiothermoluminescence is that the intensity of luminescence sharply increases (passes through maxima) in those temperature intervals in which the movement of segments of molecules or molecules as a whole begins. Radiothermoluminescence consists of the steps of irradiating the sample under study at low temperature, subsequent smooth heating of the irradiated sample, and simultaneous recording of the luminescence.

When the irradiated substance is heated, the electrons stabilized in the traps are either released or allowed to move with the trap. Such movement of traps will be accompanied by recombination of electrons with positive ions and as a consequence of it - emission of light quantum.

Recombination of ions created by radiolysis of composite, at heating of irradiated polymer, will be primarily determined by unfreezing of molecular mobility and migration of trapping centers. Not by thermal release of electron from this point of view it becomes clear why the maxima on the PTL curve are observed in the intervals of structural transitions, i.e. where there are especially rapid changes in the character of molecular mobility. Emission of light quantum at heating of irradiated polymers, as it was said above, occurs at displacement and subsequent recombination of charges stabilized on macromolecules. The charge transfer can occur by hopping between neighboring chains or along the molecular chain. In this work it is shown that

radiothermoluminescence in polymers is determined by the same motion of the polymer chain and it is assumed that recombination of charges in RTL phenomena occurs at the jump of charges from one polymer chain to another at the increase of their molecular mobility and convergence of chains with each other.

It is known that the activation energy of the process of transferring charges from one polymer chain to another is approximately an order of magnitude higher than the activation energy of the process of transferring charges along the molecular chain. Therefore, there is reason to believe that when the irradiated polymer is heated, charges move mainly along molecular chains. In this case, the mobility of the charge will be determined by the movement of the exact molecular chain on which it is stabilized. Thus, the literature review shows that the shape of the RTL curve will be determined by the nature of molecular mobility in the irradiated polymer when it is heated. In this regard, we studied the radiothermoluminescence of HDPE and HDPE+ CdS/ZnS composites with different filler content. Figure 1 shows the RTL spectra of HDPE and HDPE+CdS/ZnS composites at different CdS/ZnS filler contents. It can be seen that several highs are observed for initial HDPE at temperatures of 127, 159, 185 and 208K. The maxima observed at temperatures of 127 and 159K characterize the gamma relaxation of polyethylene, which is formed when the mobility of the side wing components of the main matrix chain increases with an increase in temperature at the initial stage. Further heating reveals two highs at temperatures

of 185 and 208K. And these maxima correspond to the characteristic β -relaxation peaks of vitrification of the main chain of the polymer matrix, i.e. HDPE.

Some changes are also observed in the RTL spectra of HDPE+CdS/ZnS composites. Thus, as the volume content of the CdS/ZnS filler increases, the maximum corresponding γ - relaxation of the polymer matrix will mix at high temperatures by approximately 6K for composites with 5% by volume and 9K for composites with 10% by volume content of CdS/ZnS. Such a change can be due both to the amount of filler and to the effect of gamma radiation during excitation. It is known that with an increase in the filler content and the effect of gamma irradiation in composites, the mobility of the molecular units of the matrix decreases due to adhesion to the surface of CdS/ZnS particles and radiation cross-linking of the matrix chains, which leads to a mixing of highs towards high temperatures.

An important feature is the high-temperature part of the RTL curves, where peaks are observed at temperatures ~ 225 – 231 K, ~ 275 – 279 K and ~ 334 – 336 K. It can be seen that the intensity of these maxima, i.e. the intensity of the glow, increases with an increase in the content of CdS/ZnS in HDPE. It is very difficult to relatively accurately determine the location of the maxima of β -relaxation processes for HDPE+CdS/ZnS composites. This is due to the mixing of the β -relaxation maximum with the maximum of the first peak of radiothermoluminescence, which appears at 226K for the composite with 5% filler, and 231K for the composite with 10% CdS/ZnS filler.

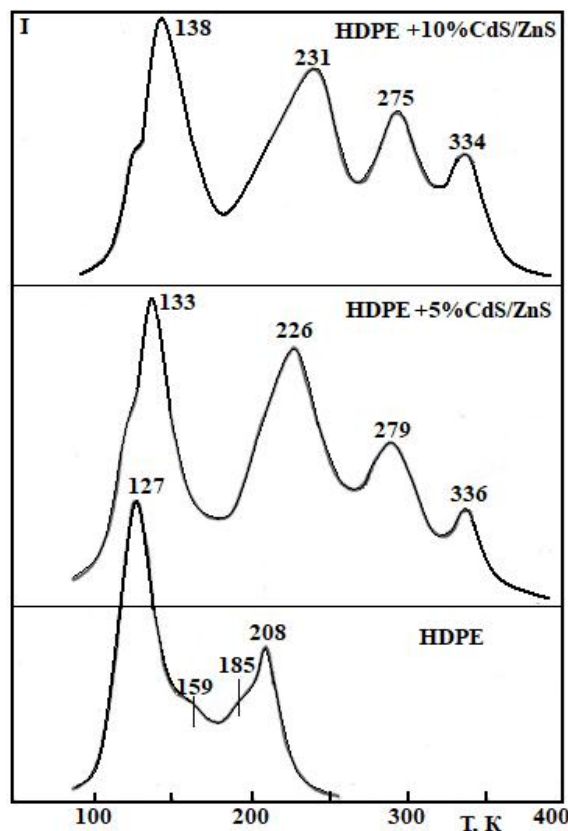


Fig. 1. RTL spectra of HDPE+CdS/ZnS composites with different filler content.

A comparison of the RTL spectra of the polymer and HDPE+CdS/ZnS composites based on it shows the appearance of three maxima at a temperature of 226, 279 and 336K for the composite with 5% filler and 231, 275 and 334K for the composite with 10% CdS/ZnS filler. At this time, the nature of these peaks is not accurate. We believe that the high-temperature peak at ~335K for HDPE+CdS/ZnS composites is due to the processes that occur in the interphase layer of the polymer matrix with the filler. We believe that the high-temperature peak at ~335K for HDPE+CdS/ZnS composites is due to the capture centers of the polymer matrix with the filler located in the interphase layer. Thus, during gamma irradiation to excite radiothermoluminescence, the created secondary electrons are captured by these centers and, when the sample is heated, they release a photon from these traps, i.e. they are luminescent. Analysis of the obtained RTL spectra of HDPE+CdS/ZnS composites suggests that the highs at the temperature range of 230–335K correspond to the luminosity of the filler. The maximum corresponding to a temperature of 226–231K, in our opinion, is the result of glow during the vitrification of the β -relaxation polymer matrix, and the maxima reproducible at temperatures of 275–279 and 334–336K are most likely the result of electron-ion processes occurring in the interphase layer of the polymer matrix with the filler after excitation by

gamma-irradiation. The table shows the values of the activation energy E_a , corresponding to each maximum of the luminosity of the polymer and composite. E_a was calculated from the temperature positions of the RTL [6] maxima corresponding to relaxation processes using the formula:

$$E_a = k \frac{AT_{\max}^2}{\Delta T_{1/2}},$$

where T_{\max} is the peak temperature value at the maximum, is the half-width of the peak, k is the Boltzmann constant, A is the coefficient, which, depending on the type of process, is taken as $1 \div 3$ [9]. The calculations made from the data obtained from the RTL spectra of the polymer and HDPE+CdS/ZnS composites are presented in Table 1.

It can be seen from the table that the activation energy value E_{a1} calculated according to the first relaxation maximum almost does not change. The activation energy E_{a2} calculated according to the second relaxation maximum for HDPE increases, and for composites with an increase in the content of filler decreases. The observed decrease in E_{a2} for composites may be associated with an increase in overvoltages (occurring mechanical destruction) in amorphous HDPE areas with an increase in the filler content.

Table 1.

Activation energy values E_a corresponding to each maximum of luminescence calculated from the RTL of polymer spectra and HDPE+CdS/ZnS composites with different filler content

sample	E_{a1} , eV	E_{a2} , eV	E_{a3} , eV	E_{a4} , eV
HDPE	0,10	0,35	–	–
HDPE-5%(CdS/ZnS)	0,08	0,18	0,32	0,75
HDPE-10%(CdS/ZnS)	0,10	0,16	0,31	0,56

The activation energy values E_{a3} and E_{a4} calculated from the third and fourth relaxation maxima show an increase of -5% (CdS/ZnS) for HDPE composites and a decrease of -10% (CdS/ZnS) for HDPE composites. We believe that the relatively increased activation energy E_{a4} for HDPE composites - 5% (CdS/ZnS) is the result of a relatively uniform distribution of filling particles across the volume of the polymer matrix. Thus, when the filling particles are evenly distributed, the effective surface of the polymer-filler mechanic phase boundary increases, which leads

to an increase in the concentration of capture centers and structural defects, and this is accompanied by an increase in the activation energy and, accordingly, the intensity of the luminescence of the composites.

Thus, based on the results obtained, we can say that the introduction of a semiconductor additive (CdS/ZnS) into HDPE leads to a change in the intensity and temperature of the maxima on the RTL curves of the composite, which can be used to predict and evaluate the luminescent, dielectric, physical and mechanical properties of composites based on them.

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