Spectral Investigations of γ-Irradiated Polyethylene/CdS+ZnS Composite Films

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Gamma-irradiated samples of the polyethylene/CdS+ZnS (PE/CdS+ZnS) composite were studied by electron paramagnet resonance and Fourier infrared spectroscopy methods. Based on the electron paramagnet resonance spectra, the nature of the induced paramagnetic radiation defects and their quantitative dependence on the absorbed dose of gamma radiation are identified. It has been established that the studied polymer composites have a higher radiation resistance in the range of absorption doses D_γ =30–100 kGy compared to pure polymer. The obtained results were confirmed by Fourier infrared spectroscopy, and it was shown that the observed changes are associated with a change in the supramolecular structure of PE/CdS+ZnS irradiated with γ-quanta.

topics: gamma irradiation, polyethylene (PE), electron paramagnet resonance (EPR) spectra, Fourier infrared (IR) spectroscopy

1. Introduction

The analysis of the literature data shows that a large number of studies devoted to the investigation of the surface and structure of polyethylene (PE) films have been carried out to date. PE films are one of the best dielectrics; their dielectric properties weakly depend on the field frequency over a wide temperature range [1, 2]. At the same time, the value of the tangent of the dielectric loss angle and dielectric permittivity noticeably increase when exposed to gamma radiation and/or accelerated electrons [3]. It has been shown that the increase in the tangent of the angle during gamma irradiation is associated with the formation of peroxide macroradicals of the terminal and middle types as a result of degradation and oxidation processes [4–6].

One of the modern and accurate methods for studying the effect of ionized radiation on polymer composites is the method of electron paramagnetic resonance (EPR), since when irradiated with hard γ-rays, paramagnetic defects are formed in composites, which cause all changes in the physical properties of the irradiated substance. In addition, by identifying the chemical nature of induced paramagnetic defects and investigating their quantitative dependence on the absorbed dose, one can determine the relationship between the change in certain physical properties, the nature and number of paramagnetic defects induced by irradiation [7–12].

Upon receiving composite materials and their irradiation, new chemical bonds and the destruction of old bonds may appear. These changes can be examined using Fourier infrared (IR) spectroscopy. Based on Fourier IR spectra, it is possible to study changes in chemical bonds in an irradiated composite.

2. Experimental part

The hot pressing method was used to obtain filled samples. Pure polyethylene was chosen as a matrix for the manufacture of composite samples. Thus, the aim of the work was to create new, more efficient polymer-sulfide CdS+ZnS composites with electret properties for electronic and converter technology and to modify these properties by ionizing radiation. In order to obtain PE/CdS+ZnS composite materials, powdered polymer (PE) and filler (CdS and ZnS) were mechanically mixed in different percentages, after which they were pressed by a hot press under a pressure of 10 MPa. The molds attached to the punches were heated to the desired temperature using heaters mounted in them.

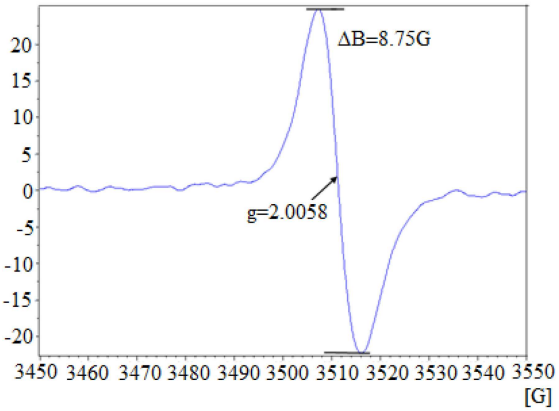

Fig. 1. EPR spectrum of PE/CdS+ZnS composite (70%:30%, 100 kGy).

Electron paramagnetic resonance experiments were carried out using a Bruker EMXplus radio spectrometer. The technical characteristics of the device are as follows:

- microwave range — X,
- microwave frequency — 9.75 GHz ($\lambda \approx 3$ cm),
- magnetic field range — 0–6000 G (0–600 mT),
- modulation frequency — 100 000 Hz,
- modulation amplitude range — 0–20 G (0–2 mT).

The EPR spectra of the samples under study were obtained in special thin-walled glass EPR tubes with an inner diameter of 3 mm, made of ultra-high purity glass, at room temperature. The spectra were taken at the optimum power of the microwave field, ~ 2.14 mW, and modulation amplitude -5 G. These parameters make it possible to avoid distortion of the spectrum shape [13].

Fourier-transform IR absorption spectra were recorded on a Varian 640 FT-IR spectrometer in the range of 4000–400 cm^{-1} at $T = 300$ K [14]. The thickness of the samples was ~ 1 μm. The samples were irradiated with a ^{60}Co isotope source with a dose rate of $dD_\gamma/dt = 182.244$ rad/s. Dosimetry of the source was carried out with ferrosulfate and methane dosimeters. The absorbed radiation dose in the systems under study was determined by comparing the electron densities [14, 15]. The radiation dose was $D_\gamma = 30$–100 kGy.

3. Experimental results and discussion

Composite samples have a composition of PE polymer and CdS+ZnS in the ratio of 70%:30%. To detect all possible paramagnetic centers, all EPR spectra of substances were taken at all possible magnetic field intervals (0–600 G). No EPR signals are observed in the unirradiated initial composite sample. After irradiation of samples of this composite

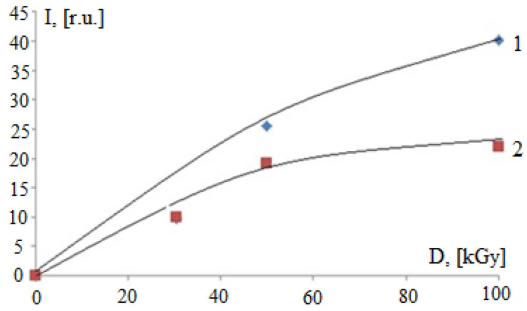

Fig. 2. Dependence of the change in the intensity of the EPR signal on the dose of radiation (1 — pure polymer, 2 — PE/CdS+ZnS (70%:30%)).

TABLE I

Dynamics of changes in the intensity of the EPR signal depending on the dose of radiation

Sample	Dose [kGy]			
	0	30	50	100
Pure polymer	0	8.5	25.5	40.2
Composite	0	8.7	19.1	21.9

with doses of 30, 50, and 100 kGy, a fairly symmetrical singlet appears in the spectrum with the parameters $g = 2.0058$ and $\Delta B = 8.75$ G (Fig. 1). The values of these parameters indicate that the unpaired electron belongs to the free radical.

This free radical is formed during γ-irradiation of the composite. Uunder the action of γ-quantum, the bond between carbon atoms (C=C) in the composition of the polymer (PE) is broken, and the resulting unpaired electron is stabilized under biographical and induced imperfections (point defects) of the polymer. The dynamics of changes in the EPR signal intensity depending on the irradiation dose for a pure polymer and a 70%:30% composite are shown in Table I and in Fig. 2 (in relative units).

In this table and graph, it can be noted that during irradiation, the intensity in both samples increases with an increase in the absorbed dose of γ-rays. In this case, this intensity (signal height) increases in the composite much more slowly. Since the intensity of the EPR signal is an indicator of the amount of free radicals formed, it can be argued that much fewer free radicals are formed in the composite compared to a pure polymer. This experimental fact suggests that the introduction of CdS+ZnS fillers into the polymer somewhat inhibits the formation of radiation paramagnetic defects and makes this composite more radiation-resistant compared to the original polymer (PE).

Figure 3 shows the Fourier IR absorption spectra of PE/CdS+ZnS samples irradiated with γ-quanta, the percentage of which was 70 wt% PE + 30 wt% CdS+ZnS. The choice of mass content of CdS and ZnS microparticles is related to the degree of crys-

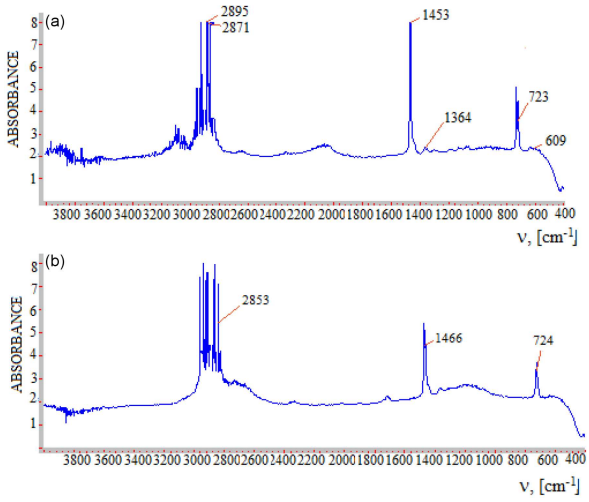

Fig. 3. Fourier IR absorption spectra of PE/CdS+ZnS (1 — pure polymer, 2 — irradiated with 100 kGy ($T = 300$ K)).

tallinity. In this case, the degree of crystallinity has a maximum value. As can be seen in Fig. 3, with an increase in the absorbed dose to 100 kGy, the intensities of the absorption bands (AB) with maxima at 724 and 723 cm^{-1} are redistributed [15, 16]. It has been established that in PE/CdS+ZnS samples, the AB intensities of the crystalline and amorphous phases change compared to the AB intensities of the initial samples. With an increase in the absorbed dose, the intensity of AB in the crystalline phase in the samples under study decreases. This shows that the studied PE/CdS+ZnS samples are more resistant to radiation, which indicates the presence of radiation defects in PE/CdS+ZnS. The formed active centers interact with the surface of microparticles, which leads to a change in the structure of PE/CdS+ZnS [15].

4. Conclusions

The possibility of using EPR and Fourier IR spectroscopy methods to study structural changes in polymer composite materials with phosphor additives under the action of γ-radiation has been shown. Using EPR spectroscopy, it was found that the introduction of the polymer composition of CdS and ZnS microparticles inhibits the formation of radiation defects, and the PE/CdS+ZnS polymer composite has a high radiation resistance compared to a pure polymer. The results obtained were confirmed by Fourier IR spectroscopy, and it was shown that the observed changes are associated with a change in the supramolecular structure of PE/CdS+ZnS irradiated with γ-quanta.

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