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EPR STUDY OF THE EFFECT OF γ-IRRADIATION ON POLYPROPYLENE/(CdS+ZnS) COMPOSITES

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A composite materials with various fillers prepared by adding cadmium sulfide (CdS) and zinc sulfide (ZnS) particles to a polypropylene (PP) matrix and irradiated with different doses of γ-rays were studied by the electron paramagnetic resonance method (EPR). The EPR spectra were investigated, and the nature of the free radicals generated from irradiation was identified. It has been shown that the concentration of radicals in the composites is much lower than in pure PP. The presence of the filler counteracts the effect of γ-rays on the formation of radicals. This result shows that the radiation resistance of the composites is higher.

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INTRODUCTION

The effect of ionizing radiation on polymers is of great interest and has been intensively studied recently [1–6]. Studying the issues of resistance to ionizing radiation effects of polyolefin polymers and composites with various fillers synthesized on their basis allows obtaining certain scientific results to ensure the long-term service of products made from these materials. In the preparation of composite materials, polymers play the role of the main matrix. By incorporating specific organic and inorganic fillers into the polymer, it becomes possible to adjust its characteristics such as flexibility, compactness, lightness, corrosion resistance, mechanical strength, ability to be formed into various geometric shapes, and radiation resistance. These adjustments enable the creation of new multifunctional composite materials with desirable electrical, optical, and magnetic properties. One of the most important issues is the study of changes in one or another physical properties of prepared composites when they are exposed to ionizing rays.

Polypropylene (PP) is one of the most widely used polymers in the preparation of composite materials. Products made of this material are often used for packaging purposes in the food industry, healthcare, and other fields and those materials are exposed to ionizing rays for sterilization. When packaging materials and other functional equipment made of PP are exposed to high-energy radiation, they degrade, resulting in changes in their morphology and alterations in their mechanical, thermal, and dielectric properties. Therefore, strengthening the radiation resistance of PP products and extending their consumption period is one of the important issues [2].

It is known that the degradation of polymers under the influence of ionizing rays occurs due to the formation of macroradicals [4]. Thus, the radiation of PP depends on the type and concentration of radicals formed as a result of irradiation. The addition of various fillers to the polymer to reduce the amount of generated radicals, by creating traps that catch radicals inside it and thereby slowing down the degradation of the polymer is of particular interest.

To obtain new electret, electrophysical, and other properties, various dispersed fillers are added to the polymer volume. In this direction, the creation of new composite materials based on polyolefins and phosphor fillers is one of the promising tasks of radiation materials science. When the CdS+ZnS phosphor is introduced into PP, the supramolecular structure changes and new polar groups and stable traps for electric charges appear in the composite, which leads to an increase in the dielectric constant and polarizable ability of the polymer. These materials are widely used in microelectronics, dosimeters, spacecraft, pressure sensors, etc., where they can be exposed to ionizing radiation. Therefore, studying the effect of γ-rays on these composites is of certain interest from the point of view of determining their radiation resistance.

Our article is devoted to finding out what happens during γ-irradiation of the new composites we have obtained, what radicals are formed in them, how their amount changes from the absorbed dose, and how all this is reflected in their radiation resistance.

In this work presented, the identification of radicals formed under the influence of γ-rays in pure PP (PP100%) and in two composites (70%PP/30%(CdS+ZnS), 50%PP/50%(CdS+ZnS)), and also the dependence of their concentration of the amount on the absorption dose of radiation rays and the percentage of the filler was investigated by the electron paramagnetic resonance method (EPR). The goal is to study how the radiation resistance of the composite material changes compared to the pure polymer.

1. MATERIALS AND METHODS

The samples for the study were obtained by hot pressing a mixture of polymer powders and filler in a hydraulic press with heaters. The technique for obtaining composite samples, both the original PP and composites based on it, was as follows:

– mechanically mixing powdered phosphor additives with PP powder in a porcelain mortar until a homogeneous mixture is obtained;

– the mixture located between two aluminum foils and a gasket with a thickness of 100 μm is maintained for some time at the melting temperature of the polymer under low pressure (1 MPa);

– at the same temperature, the pressure slowly rises to 10 MPa at which the sample is kept for 5 min, then the pressure is removed and the sample is quickly cooled in a water-ice mixture;

– the dimensions of the materials were: thickness in the order of 100...120 μm, the diameter of the resulting round thin sheets was 45 mm.

The main ɣ-radiation sources were isotope installations of the K-25 or MRKh-ɣ-25M type based on ^{60}Co with a half-life of 5.3 years and an emitter activity of $5 \cdot 10^4$ Ci at a temperature of 293 K.

The EPR spectra of the studied substances were recorded at room temperature on the EMX Plus radio spectrometer manufactured by the “Bruker” company. The spectrometer works in the X-band of the microwave, the frequency is 9.85 GHz (wavelength λ~3 cm), and the maximum magnetic interval is 0...6000 Gs. Measurements were conducted by cutting samples 10 long and 2 mm wide from thin sheets and filling them in special EPR tubes made of thin-walled ultra-pure glass. In acquiring the EPR spectra, the modulation frequency was set to 100 kHz. Both the modulation amplitude and the microwave power were carefully adjusted to ensure optimal signal quality and accurate data acquisition.

2. RESULTS AND DISCUSSION

EPR spectra of all three materials were recorded in the widest interval of the magnetic field 250...5750 Gs to obtain information about the presence of paramagnetic centers in the initially non-irradiated samples.

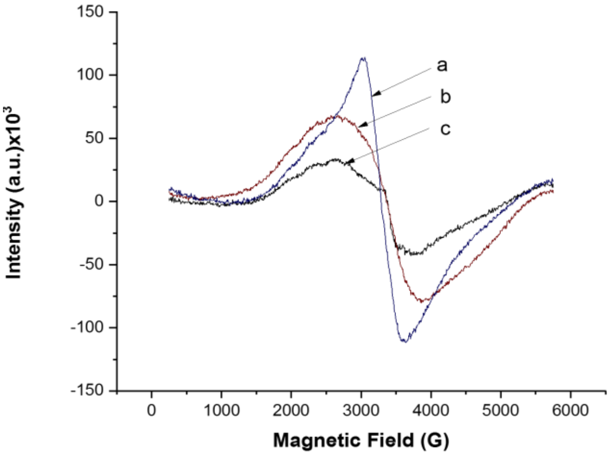

Fig. 1. EPR spectra of non-irradiated samples: a – pure PP100%; b – 30% composite; c – 50% composite

It can be seen from Fig. 1 that a broad singlet line is observed in the region of g~2.00 in all three spectra. The values of spectral parameters and intensities of these lines are shown in Table 1.

As shown in Table 1 and indicated by the spectral forms, the g-factor values for the samples vary slightly around 2.00. However, the line widths nearly double when transitioning from pure PP to composite materials. At the same time, as the percentage of the fillers in the composites increases, the intensity of the line decreases. The absence of individual lines from other paramagnetic centers in addition to the line observed in all three spectra indicates that the studied samples are highly free of other paramagnetic impurities.

Table 1

The values of spectral parameters and intensities of lines in non-irradited samples

Material	g-fak-tor	ΔB, Gs	İ (a.u) – intensity (pik to pik)
100%PP	2.1476	620	222.600
70%PP/ 30%(CdS+ZnS)	2.0990	1260	145.963
50%PP/ 50%(CdS+ZnS)	2.0963	1135	74.621

The changes in both the g-factor and line width in the composites suggest that CdS+ZnS particles infiltrate the spaces between polymer chains, altering the chemical composition, geometrical structure, and symmetry of the immediate environment of the paramagnetic centers. In the samples exposed to γ-rays, at the same range of the magnetic field a new, very intense thin signal is detected at the region g~2 at the applied absorption doses in the EPR spectra (Fig. 2).

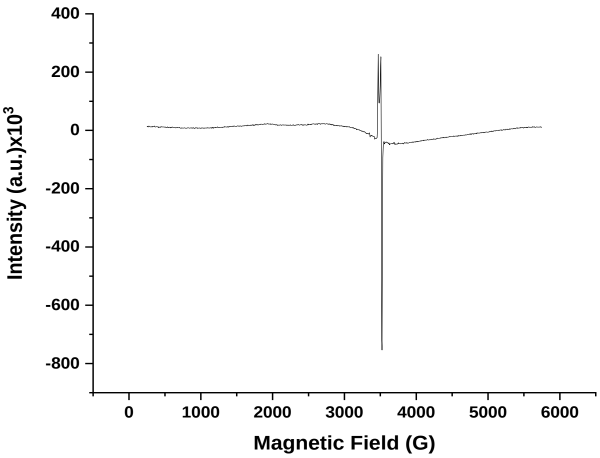

Fig. 2. EPR spectrum of an irradiated 50%PP/50%(CdS+ZnS) sample

This signal indicates the presence of newly formed paramagnetic centers within the polymer matrix as a result of γ-ray irradiation. To determine the spectroscopic parameters of this spectrum, this central signal was recorded in a smaller interval of the magnetic field (Fig. 3).

It was studied how the intensity of the spectrum of this signal caused by the influence of γ-rays changes depending on the radiation dose and the composition of the substance (Table 2). It can be seen from Table 2 that the intensity of the spectral line for all three substances increases sharply depending on the absorption dose. Also, this intensity increase is almost twice as high in pure PP than in composites.

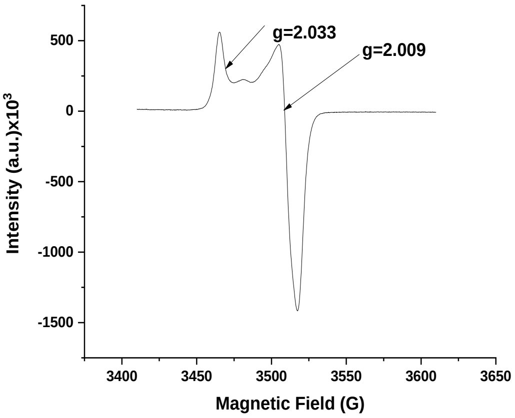

Fig. 3. EPR spectrum of the irradiated sample

Table 2

The intensity of the spectrum of the signal caused by the influence of γ-rays

Material	Intensity (a.u.)		
	30 kGy	50 kGy	80 kGy
100%PP	1.00	2.45	5.63
70%PP/ 30%(CdS+ZnS)	0.62	0.88	1.53
50% PP/ 50%(CdS+ZnS)	0.65	1.25	1.82

It can be seen from Table 2 that for all three absorption doses, the line intensity in the composites is significantly reduced compared to pure PP. As the dose increases, the decrease in the intensity of the line is sharper in composites than in pure PP. This decrease suggests that the CdS+ZnS filler in the composite material inhibits the formation and stabilization of paramagnetic centers, which are the sources of this spectral line. In a special case, in the 50%(PP)/50%(CdS+ZnS) composite, three slightly smaller intensity lines with equal intensities located at a distance of 67.5 Gs are observed in the spectra (Fig. 4).

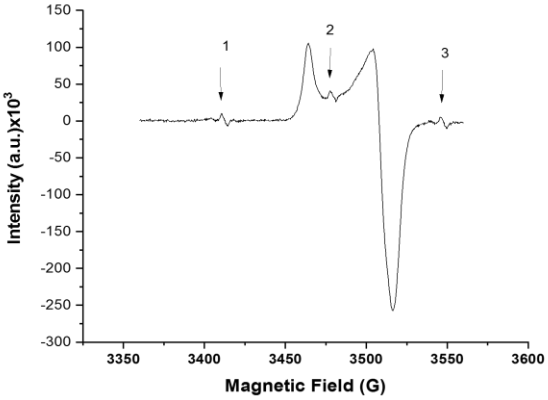

Fig. 4. EPR spectrum in 50%(PP)+50%(CdS+ZnS) composite

The observation of three equidistant lines (triplet) of equal intensity, marked with arrows in the spectra of the 50% composite samples, suggests that this composite has a low concentration of paramagnetic centers with a nuclear magnetic moment of I=1.

The properties of composite materials depend on the characteristics of the polymer that makes it, the filler that creates the composite, and the phase space of these constituents. The parameters of the EPR spectrum of the paramagnetic centers formed in these materials depend on the details of the chemical relationships: the chemical composition of the immediate surroundings of the unpaired electron, and the symmetry of the surrounding structure.

The broad EPR spectra discussed above are commonly observed in commercially produced polymers [7]. In this study, EPR spectra with very large line widths were observed in crosslinked polyethylene (XLPE) and SiO_2/XLPE composites. Since the width of the lines is very large, the exact values of the g-factor and the width of the line have not been determined. However, since the peaks corresponding to the maximum in the low magnetic field of the lines are more obvious, those individual lines have been named lines with a maximum of 3000 and 2600 Gs. The chemical source of these signals has been proposed to be the 5-oxygen radical (1):

$$O(\bullet)\text{-}O(\bullet)\text{-}O(\bullet)\text{-}O(\bullet)\text{-}O(\bullet). \quad (1)$$

Here (•) indicates the unpaired electron associated with the EPR-active oxygen atom.

During the polarization of the electric field around the electron, the possibility of the formation of the second type (2) radical was accepted:

$$O(\bullet)\text{-}O(\bullet)\text{-}O(\bullet)\text{-}O(\bullet)\text{-}O(\bullet\bullet). \quad (2)$$

In the first case, the relative intensity of the EPR spectrum corresponds to 5, while the relative intensity of the second radical should correspond to 3. It is well known that during normal polymer processing, oxygen radicals formation is happening and in this case, peroxides are added to aid in cross-linking which certainly introduces oxygen to the system [7].

From the EPR spectra of unirradiated PP and composites (see Fig. 1), it is easy to see that pure PP exhibits a slightly asymmetric signal with a maximum of around 3000 Gs and a width of Δ~620 Gs. When moving to 30 and 50% composites, a new line is observed with a maximum of around 2600 Gs and a width approximately 2 times greater than that of pure PP. In contrast to work [7], spectral lines are more clearly observed in the samples studied by us, and this allowed us to show the approximate values of spectral parameters and line intensities for all three samples (see Table 1). The change of the g-factor and line width of the EPR spectrum in composites compared to pure PP is the result of the change of the parameters of the interfacial space between the polymer chains as a result of the introduction of the filler into the polymer. As a result of the change of the parameters of this field, the dominance of the individual line with the maximum at 2600 Gs may be an indicator of the transition from radicals with 5 unpaired electrons to radicals with 3 unpaired electrons. The decrease in the intensity of the EPR spectrum in the composites compared to pure PP confirms this result.

In the spectra of the irradiated samples, a spectral line has axial symmetry with completely identical spectral parameters was formed in both pure PP and composites, and the very broad line observed in the non-irradiated samples appeared with almost too little intensity (see Fig. 3). The obtained values for the g-factors of this line ($g_{||}$=2.033, $g_{\perp}$=2.009, and g_{aver}=2.017) are very characteristic for PP polymer, and the paramagnetic center with these parameters has stability at room temperature [1].

It is known that free radicals are formed due to the breaking of chemical bonds under the influence of high-energy radiation, which leads to chemical transformations within the polymer, oxidation in the air, and subsequent chain breakage reactions. These modifications in the polymer depend on the dose rate of the radiation source, the absorbed dose, temperature and atmospheric conditions. The selected absorption doses (30, 50, 80 kGy) in the experiments conducted in this work were close to the dose range (20...50 kGy) applied during the sterilization of polymer containers and food products, and the experiments were conducted at room temperature under atmospheric conditions.

Alkyl-type and allyl radicals are initially formed in PP as a result of irradiation [1]. The formed alkyl radicals react with the dioxygen molecule to form an alkylperoxyl radical (R-O-O(•)).While this alkylperoxyl radical can remain stable for a long time at room temperature, alkyl, and allyl-type macroradicals undergo recombination and oxidation as a result of mobility at room temperature and disappear. Since the spectral parameters of the EPR spectrum shown in Fig. 3 ($g_{||}$=2.033, $g_{\perp}$=2.009) and the shape of the spectrum completely coincide with the spectrum presented in [1], we can confirm that the source of the EPR spectrum founded in the PP and composite samples studied by us are the alkylperoxyl radical (R-O-O(•)) formed in the material.

The oxidative degradation of polyolefins due to radiation exposure is closely related to the number of peroxyl radicals formed in them and the concentration of oxygen [8].

Since spectral parameters and axial shape of alkylperoxyl radicals formed as a result of sample irradiation are identical for all samples, it can be confirmed that only original carbon radicals and dioxygen molecules formed in PP chains participated in the generation of R-O-O(•) radicals both in pure PP and in composites. In the composites, fillers did not affect the formation reactions of these radicals. The absence of any signal in the EPR spectrum, in addition to the line belonging to R-O-O(•), indicates that neither the additives in the PP-matrix, nor the particles formed in them due to the effect of radiation, were not EPR active.

İt is known that the intensity of the spectra (peak to peak) is proportional to the number of free radicals and so the concentration of alkylperoxyl radicals increases as the absorption dose increases for all three samples (see Table 2). In composites, the concentration of stabilized radicals is much lower than in pure PP, and as the absorption dose increases, this reduction becomes higher. A significant reduction of alkylperoxyl radicals in composites is considered the reason an indicator of higher radiation resistance of composites [2].

The main role in obtaining composites with physical properties different from the pure polymer is played by the interfacial space between the filler and the polymer chain (interaction zone) [5, 9]. Thus, in this interfacial space, certain interactions between filler particles and polymer atoms take place: chemical bonds are formed and the modification of the polymer undergoes significant changes. These changes, in turn, lead to two events: i) carbon radicals formed in the polymer chain as a result of irradiation are actively captured by filler particles (scavenging); ii) as a result of the modification of the polymer structure, the interfacial space becomes both narrow and significantly tortuous, which makes it much more difficult for dioxygen molecules to enter the polymer [2]. As a result, the number of both carbon radicals involved in the formation of active peroxyl radicals and dioxygen molecules reacting with them decreases. This leads to a significant reduction of R-O-O(•) radicals in composites compared to pure PP, and thus the radiation resistance of composites increases significantly.

In Fig. 4, the observation of three lines with the same intensities in the EPR spectrum of the alkylperoxyl radical in the 50% composite sample and the field distance between them can be explained by the fact that there is another paramagnetic center in this substance with the nuclear spin I=1, and as a result, a superfine triplet structure appeared. The chemical source of this triplet is most likely nitrogen atoms as an impurity of filler.

CONCLUSIONS

Pure PP polymer and two 70%PP/30%(CdS+ZnS) and 50%PP/50%(CdS+ZnS) composites were studied by EPR method. The broad spectral line observed in non-irradiated substances was attributed to oxygen radicals containing 3 and 5 unpaired electrons. The problem of resistance of the studied substances to ionizing rays was considered. It was found that alkylperoxyl (R-O-O(•)) radical with identical spectrum is formed in all three materials under the influence of γ-rays. The dependence of the concentration of the generated radicals on the absorption dose of γ-rays was studied and it was found that the concentration of radicals in composites is much lower than in pure PP. This result shows that the radiation resistance of the composites is higher. The role of the interfacial space in reducing the number of radicals was investigated.

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ЕПР-ДОСЛІДЖЕННЯ ВПЛИВУ γ-ОПРОМІНЕННЯ НА КОМПОЗИТИ ПОЛІПРОПІЛЕН/(CdS+ZnS)

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Методом електронного парамагнітного резонансу (ЕПР) вивчено композиційні матеріали з різними наповнювачами, які отримані додаванням частинок сульфіду кадмію (CdS) та сульфіду цинку (ZnS) до поліпропіленової (ПП) матриці та піддані опроміненню різними дозами γ-променів. Досліджено спектри ЕПР та встановлено природу вільних радикалів, що утворюються при опроміненні. Показано, що концентрація радикалів у композитах значно нижча, ніж у чистому ПП. Наявність наповнювача протидіє впливу γ-променів на утворення радикалів. Цей результат свідчить, що радіаційна стійкість композитів вище.