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STUDY OF γ-IRRADIATED POLYETHYLENE TEREPHTHALATE POLYMER BY EPR METHOD

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Non-irradiated and irradiated in a vacuum with ^{60}Co γ-rays at various absorption doses samples of waste polymer Polythylene terephthalate (PET) were studied at room temperature using an X-band electron paramagnetic resonance (EPR) radiospectrometer. The paramagnetic centers responsible for the spectral lines observed in the EPR spectra were identified, and the mechanism for the intensity variation of EPR spectra with different absorption doses was explained. The nature and structure of macroradicals in PET samples were determined, revealing that the chemical source of the observed EPR spectrum is cyclohexadienyl type macroradicals formed under the influence of γ-rays in the polymer chain.

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INTRODUCTION

The impact of ionizing radiation on polymer materials results in changes to their physical and chemical properties, primarily due to the formation of defects of various types within these substances. Recently, numerous researchers have focused on studying the effects of γ-irradiation on original polymers, their mixtures, and composite materials [1-4]. Exposure to γ-rays causes the rupture of polymer chains and the formation of free macroradicals. This process leads to either a restructuring of the chemical structure or oxidation in the presence of air, as well as cross-linking.

The nature, properties, and mechanisms of radiation-induced defects in polymers have been extensively studied using various methods, including UV, IR, EPR spectroscopy, chromatography, SEM, and TEM [4–7]. Among these, the EPR method holds particular significance for investigating the chemical sources of paramagnetic defects in polymer materials. EPR spectroscopy has been used to determine the nature of paramagnetic centers and their radiation-chemical yield in various types of polymers exposed to ionizing radiation. It has been shown that the characteristics of these paramagnetic centers and their radiation-chemical yield are influenced by factors such as the polymer's structure, chemical composition, radiation source power, and temperature conditions.

In today's context, the recycling of plastic waste is of paramount importance. The parameters observed during the reuse of these wastes (viscosity, radiation resistance, mechanical and electrical properties, e.g.) differ from those of initial polymer materials. Therefore, studying plastic waste exposed to ionizing radiation is a pressing issue. Polyethylene terephthalate widely used in packaging constitutes a significant portion of plastic waste by volume, making its investigation particularly relevant.

This study aims to determine the nature of macroradicals formed in industrially produced PET plastic waste as a result of exposure to γ-rays at various absorption doses and to examine the relationship between their concentration and the absorption dose.

1. EXPERIMENTAL PART

The following table shows the physical and chemical properties of Polyethylene Terephthalate [8].

Table1

The physicochemical properties of PET-1 brand Polyethylene terephthalate polymer wastes

Molar mass	10…50 kg/mol, varies
Density	1.38 g/cm^3, 20 °C 1.370 g/cm^3, amorphous 1.455 g/cm^3 single crystal
Melting point	> 250 °C
Boiling point	> 350 °C (decomposes)
Solubility in water	It is practically insoluble
log P	0.94540
Refractive index (nD)	1.57…1.58; 1.5750
Young's modulus, E	2800…3100 MPa
Tensile strength, σt	55…75 MPa
Elastic limit	50…150%
Notch test	3.6 kJ/m^2
Glass transition temperature, Tg	67…81 °C
Vicat B	82 °C
Water absorption (ASTM)	0.16

Samples were irradiated using a ^{60}Co γ-ray source (MRX-γ-25) with a dose rate of P=0.99 Gy/s and absorption doses of 32…1500 kGy. EPR spectra were obtained using an EMX Plus radiospectrometer from "Bruker", operating in the X-band (ν ≈ 9.8 GHz) with a magnetic field range of 0…6000 G and a modulation frequency of 10^5 Hz. Transparent samples of polymer waste were prepared in the form of plates measuring approximately 1 cm in length, 1…2 mm in width, and 0.1 mm in thickness. These samples were irradiated in a

vacuum and then placed in special EPR tubes with an internal diameter of 3 mm and the spectra were recorded under air conditions and at room temperature. To obtain accurate spectra, the microwave power and modulation amplitude were optimally selected.

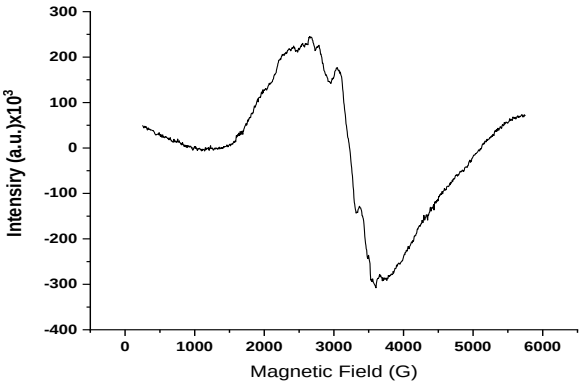


Fig. 1. EPR spectrum of non-irradiated samples

In the EPR spectra of non-irradiated samples, only a very broad line with a width of ΔB≈1100 G and a g-factor of g≈2.157 is observed (Fig. 1). For samples that received a dose of 95 kGy or more, a second, thinner line with a g-factor of g≈2 is formed, with its intensity increasing as the dose increases (Fig. 2).

The intensity of the broad line remains almost unchangeable regardless of the absorbed dose. This constancy suggests that the paramagnetic centers responsible for this broad line were formed prior to irradiation and are unaffected by ionizing radiation. These centers likely result from their uneven creation and distribution during the polymer production process. It has been shown that the chemical source of this spectral line is oxygen radicals [2]. The changes in the intensity of the thin lines in the spectra, depending on the absorption dose, are detailed in the following Table 2.

The increasing intensity of the thin line with higher absorption doses indicates that the paramagnetic centers responsible for these spectra are formed under the influence of ionizing radiation. In non-irradiated samples and those with an absorbed dose of 32 kGy, this thin line is practically absent. However, starting

2. EXPERIMENTAL RESULTS AND DISCUSSION

The typical EPR spectra of non-irradiated and irradiated samples are shown in Figs. 1, 2 accordingly.

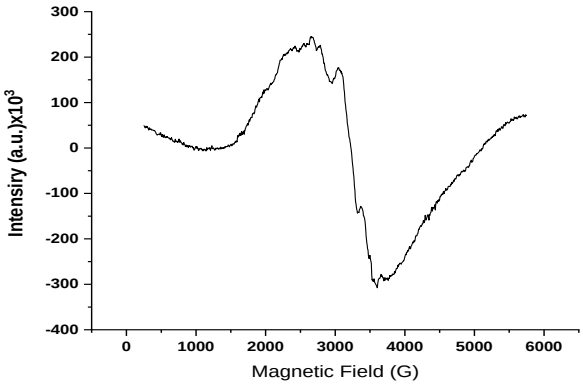


Fig. 2. EPR spectrum of samples at 794 kGy

from a dose of 95 kGy, the intensity of this peak increases significantly at higher doses. The spectral line parameters indicate that the spectrum is due to free radicals, as the g=2.005 value is characteristic of free radicals.

Table 2

Dose dependence of thin line intensity

Dose, kGy	Intensity, a.u.
0.00	0
32.00	0
95.00	15.680
190.00	25.189
794.00	140.255
1.000.00	64.168
1.500.00	68.027

In such macroradicals formed in polymers, the unpaired electron is localized on the carbon atom, appearing as a result of hydrogen atom cleavage or C–C-bond cleavage within the polymer chain.

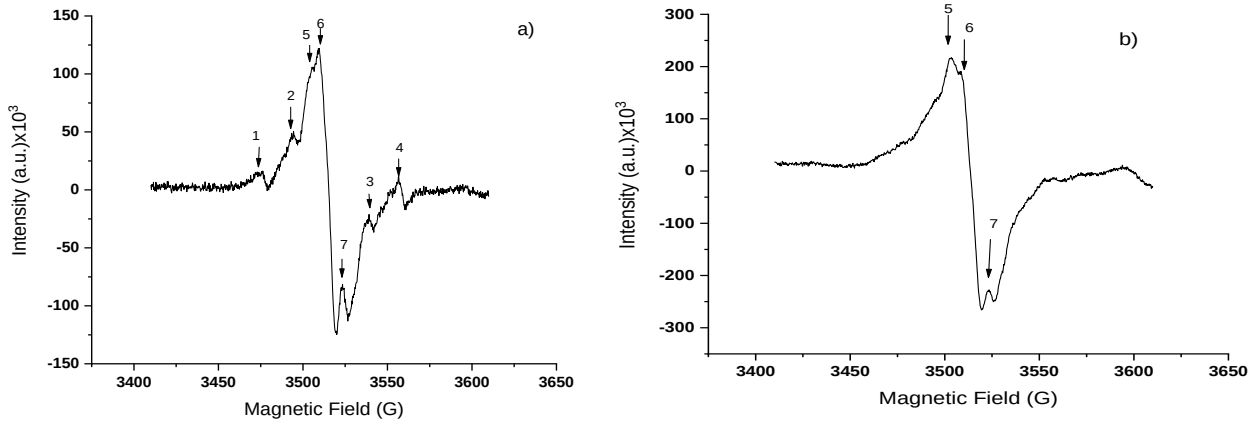


Fig. 3. EPR spectra of PET samples at 794 kGy in the thin line area: a – microwave power 0.067 mW, b – microwave power 2.170 mW

It is known that the degradation of polymers under γ-rays is closely related to macroradical formation, leading to significant mechanical, thermal, electrical, and other damages to polymers [6, 7].

The table shows that radical concentration peaks at an absorption dose of 794 kGy, then decreases slightly at higher doses. This decrease might be attributed to enhanced processes of radical capture and recombination at higher doses.

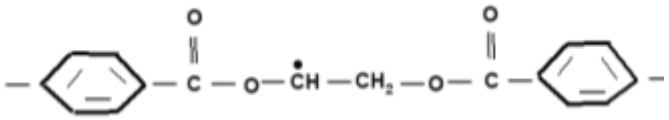
To further explore the chemical nature and structure of the macroradicals, the spectral line attributed to them was studied separately. The thin line part of the spectrum was recorded over a smaller magnetic field region (200 G), and changes in these spectra were observed at two different microwave powers (Fig. 3).

In Fig. 3,a, two groups of peaks can be distinguished. Peaks 1, 2, and 3, 4 are located symmetrically around peaks 5, 6, 7 in the center. The distance between peaks 1 and 2 is equal to the distance between peaks 3 and 4, and at high microwave power, peaks 1, 2, 3, and 4 practically disappear simultaneously (see Fig. 3,b). Additionally, the distance between peaks 1–2 and 3–4 is the same (≈18 G), suggesting that the chemical source of peaks 1, 2, 3, and 4 is the same, and these lines are the superfine structure lines of this source.

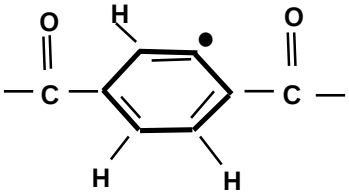
It is known that macroradicals of the alkyl and allylic types are formed in polyolefin-containing polymers under the influence of ionizing radiation, where the unpaired electron is localized on the carbon atom and interacts with the nuclei of hydrogen atoms, giving EPR spectra with a superfine structure [6].

As a result of hydrogen atom abstraction from the $–CH_2–CH_2–$chain, radicals similar to alkyl-type radicals and stable at room temperature can be formed in the PET molecule. Peaks 1, 2, 3, and 4 can be attributed to radicals arising from the $–CH_2–CH_2–$ group in the molecule. The structure of these radicals is shown below in form (I) in [9].

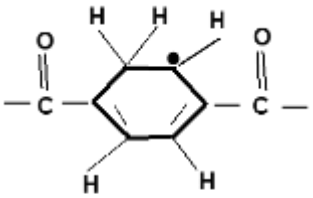
In Fig. 3,b, it is easy to see that at a microwave power of 2.170 mW, peaks 1, 2, 3, and 4 from Fig. 3,a disappear, and a triplet consisting of three (5, 6, 7) lines are observed in the center. The intensity of the line in the middle of the triplet is at least twice that of its two outer satellites, and the superfine constant of the triplet is approximately 10 G. The chemical source of this spectrum was proposed in form (II) in [9]; and as a cyclohexadienyl-type radical in form (III) in [10].



(I)



(II)



(III)

In the EPR spectrum, two triplets are observed for the radical type in form (II), with no lines in the central part, and for the radical type in form (III), three triplet lines are observed, with the more intense lines of this triplet located in the center [9, 10].

Since lines 5, 6, 7 in the center of Fig. 3,b form a triplet, it can be confirmed that these peaks belong to cyclohexadienyl radical type in form (III). Since the signals of this radical in the lower and upper parts of the magnetic field relative to the center are very weak, they are not observed in the spectrum, as in [10].

CONCLUSIONS

EPR spectra of samples of commercial Polyethylene terephthalate polymer were studied by irradiating them with different doses of γ-rays. As a result of the analysis of the spectra, it was found that only two types of radicals are observed in the samples: oxygen and carbon radicals. It has been shown that oxygen radicals are formed during polymer synthesis, and carbon radicals are formed by ionizing γ-rays. It was found that two types of carbon radicals were observed. One of them is of the alkyl type, and the other is a cyclohexadienyl type radical.

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REFERENCES

1. M. Roy, J.K. Nelson, R.K. MacCrone, L.S. Schadler, C.W. Reed, R. Keefe, and W. Zenger. Polymer nanocomposite dielectrics-the role of the interface // *Trans. IEEE.* 2005, v. 12, p. 629-643.

2. R.K. MacCrone, J.K. Nelson, L.S. Schadler, R. Smith, and R. Keefe. The use of Paramagnetic Resonance (EPR) in the probing of the nanodielectric interface // *Arhcle in IEEE Transaction on Dielectrics and Electrical Insulation-March 2008*.

3. I.I. Mustafayev, S.Z. Melikova, E.G. Hajiyeva, R.J. Gasimov, M.A. Bayramov, N.I. Babayeva. Spectral Investigations of γ-Irradiated Polyethylene/CdS+ZnS Composite Films // *Acta Physica Polonica A.* 2023, v. 144, N 1.

4. M.A. Gurbanov, R.J. Gasimov, E.V. Mirzazada, U.A. Guliyeva. Study of the effect of γ-irradiation on Polypropylene and Polystyrene wastes by EPR method // *Journal of Radiation Researches*. 2023, v. 10, N 2, p. 57-64.

5. L.M. Rincon-Rubio, B. Fayolle, l. Audoin, J.Verdi. A general solution of the closed – loop kinetic scheme for the Thermal of polypropylene // *Polim. Degrad. Stable.* 2001, v. 74(1), p. 177-188.

6. E. Fel, L. Khrouse, V. Massarder, L. Bonnevoit. Comparative study of gamma-irradiated PP and Polyolefin. Part1: Identification and quantification of radicals using electron paramagnet resonance // *Polymer*. 2015, v. 77, p. 278-288.

7. Y. Lin, Y. Liu, D. Zhang, G. Wu. Radiation resistance of polypropylene composites by incorporating reduced graphen oxide and antioxidant: A comparison study // *Composites Science and Technology*. 2017, v. 146, p. 83-90.

8. Report of IAEA Technical Meeting. EVT1804861.30.09.–04.10.2019. Vienna, Austria, 2019, p. 21.

9. D. Compbell, K. Araki, D. Turner. Elementary processes in the radiation-induced degradation of poly(ethylene terephthalate) // *Polymer Sci. A.* 1966, v. 1, N 4, p. 2597.

10. M. Mariani, U. Ravasio, G. Consolati, A. Buttafara, M. Giola, A. Fauctiana. Gamma irradiation of Polyethilen Terefthalate and Poliethilene Naphalate // *Nucliear Instruments and Metals in Physics Research B.* 2007, v. 265, p. 245-250.

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ДОСЛІДЖЕННЯ γ-ОПРОМІНЕНОГО ПОЛІЕТИЛЕНТЕРЕФТАЛАТУ МЕТОДОМ ЕПР

М.А. Гурбанов, Р.Й. Гасімов, М.А. Байрамов, У.А. Гулієва, Є.В. Мірзазада

Неопромінені та опромінені у вакуумі γ-випромінюванням ^{60}Co при різних дозах поглинання зразки відходів полімерного поліетилентерефталату (ПЕТ) досліджували за кімнатної температури за допомогою радіоспектрометра електронного парамагнітного резонансу (ЕПР) X-діапазону. Виявлено парамагнітні центри, відповідальні за спектральні лінії, що спостерігаються у спектрах ЕПР, і пояснено механізм зміни інтенсивності спектрів ЕПР за різних доз поглинання. Визначено природу та структуру макрорадикалів у зразках ПЕТ, виявивши, що хімічним джерелом спостережуваного спектра ЕПР є макрорадикали циклогексадієнільного типу, які утворюються під впливом γ-променів у полімерному ланцюзі.