*https://doi.org/10.46813/2025-159-028*

# GAMMA IRRADIATION INDUCED STRUCTURAL MODIFICATIONS OF HDPE POLYMER AND HDPE/GaAs<Te> COMPOSITE FILMS

***N.N. Gadzhieva[1], G.B. Akhmedova[2], R.A. Mammadov[1]***
***[1]Institute of Radiation Problems of Ministry of Science and Education Republic of Azerbaijan, Baku, Azerbaijan;***
***[2]Institute of Physics of Ministry of Science and Education Republic of Azerbaijan, Baku, Azerbaijan***
***E-mail: nushabafereh@gmail.com***

This paper presents the results of an FTIR spectroscopy study on the physical and chemical structural modifications induced by gamma irradiation in HDPE polymer and HDPE/GaAs<Te> composite films in absorbed dose range of $\Phi_\gamma = 50…350$ kGy. It has been shown that gamma irradiation causes changes in the degree of crystallinity and the formation of polyene (–C=C–) and carbonyl (C=O) groups in polymer and composite films. The dose dependencies for these modifications exhibit a similar trend, indicating a direct relationship between the degree of crystallinity and the crosslinking process. Comparative analysis confirms that composite films are more radiation-resistant than the polymer films.

PACS: 77.-55.-g

## INTRODUCTION

Currently, issues related to the effects of ionizing radiation on polymers and their composites are of significant interest and the subject of extensive research efforts [1–5]. Studies of structural changes occurring under the influence of ionizing radiation, including gamma radiation, as well as investigations into various properties of polymer-semiconductor composites using modern optical-luminescent and electro physical methods, have demonstrated the possibility of obtaining new radiation-resistant composite materials with modified structures and controlled properties [6–11].

Radiation-induced structural modifications in these materials impose limitations on their exposure to ionizing radiation. In certain applications, it is essential that polymer composites withstand radiation without undergoing structural degradation that modifies its properties.

Among polymer–semiconductor composites, HDPE (high-density polyethylene) / GaAs (GaAs<Te>) composites are of particular interest, as HDPE is multifunctional and well-studied polymer, while GaAs and GaAs<Te> semiconductors exhibit effective radiation resistance (in particular, GaAs is widely used as a neutron detector), which expands their potential applications [5–7].

As previous studies have shown [12–14], the structural modification of HDPE polymers under the influence of gamma radiation strongly depends on the formation processes of crosslinking and chain scission. It has been established that during irradiation, there is a balance between these two processes, controlled by the structural properties of the polymer [15, 16]. The processes of scission and long macromolecular chains, as well as crosslinking of intermolecular and interchains are typically observed in different radiation doses. It should be noted that chain scission occurs throughout the entire irradiation process while simultaneously competing with crosslinking. The ratio of crosslinking to chain scission depends on radiation power and dose, crystallization and oxidation degrees, and various other specific material characteristics [17, 18].

It should be noted that structural modifications induced by gamma irradiation in HDPE polymer and HDPE/GaAs composite films have been studied using Fourier-transform infrared (FTIR) spectroscopy, with results reported in [7]. Therefore, the present work focuses on the FTIR spectroscopy investigation of gamma irradiation-induced physical and chemical structural modifications in HDPE polymer and HDPE/GaAs<Te> composite films within an absorbed dose range of $\Phi_\gamma = 50…350$ kGy, at room temperature in air. The dose dependences of the relative crystallinity before and after irradiation (physical modification) and of the optical densities of the characteristic polyene (–C=C–) and carbonyl (C=O) group bands (chemical modification) in both polymer and composite films were obtained. Based on their comparative analysis, the regions corresponding to crosslinking and scission processes were identified, and the radiation resistance of the materials was evaluated.

## 1. EXPERIMENTAL PART

High-density polyethylene (HDPE) powder (Russia, Kazan) with a melting point of 130 °C and a density of 947 kg/m³ was used as the polymer matrix. According to X-ray diffraction (XRD) analysis, HDPE exhibits an orthorhombic structure [9]. GaAs and GaAs<Te> semiconductors of the $A^3B^5$ type were used as fillers. HDPE, HDPE/GaAs, and HDPE/GaAs<Te> films were obtained using the method described in [1, 2].

HDPE, HDPE/GaAs, and HDPE/GaAs<Te> films with a thickness of ~100 μm were irradiated by γ-radiation using an MRX-γ-20 ($^{60}$Co) gamma source (Azerbaijan, Baku) at an exposure rate of $d\Phi_\gamma/dt$ = 1.06 Gy/s. The samples were irradiated in an absorbed dose range of $\Phi_\gamma = 50…350$ kGy.

FTIR transmission spectra of these films were recorded using a Varian 640 FTIR spectrometer at room temperature in the frequency range of

ν = 4000…400 $cm^{-1}$. The spectra were obtained for both the polymer and composite films as a function of the wavenumber.

The optical densities of the transmission bands corresponding to polyene (–C=C–) and carbonyl (C=O) vibrations, with maxima at ν = 1650 $cm^{-1}$ and ν = 1715…1735 $cm^{-1}$ respectively, were determined.

The dose dependencies of the optical density of the (–C≡C–) and (C=O) transmission bands, as well as the relative degree of crystallinity, were obtained for HDPE polymer and HDPE/GaAs<Te> composite films, and their characteristics were analyzed.

## 2. RESULTS AND DISCUSSION

### 2.1. CHEMICAL STRUCTURAL MODIFICATION

Figs. 1 and 2 show the FTIR transmission spectra of initial and gamma irradiated HDPE polymer and HDPE/4 mass% GaAs<Te> composite films.

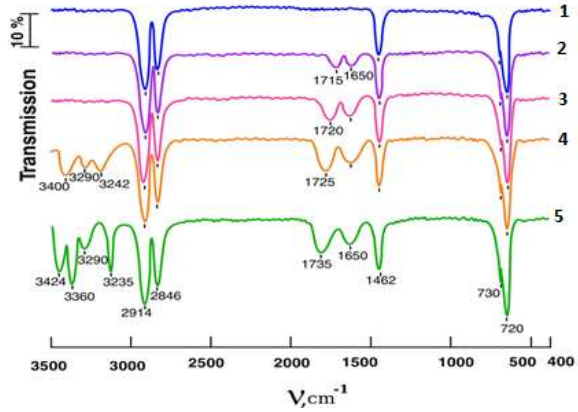


*Fig. 1. FTIR – spectra of initial and gamma irradiated HDPE films: HDPE (1); 50 (2);150 (3); 250 (4), and 350 kGy (5)*

The choice of the 4 mass% content of GaAs and GaAs<Te> microparticles is based on the fact that at this concentration, the degree of crystallinity remains same (K = 68%) [1, 4].

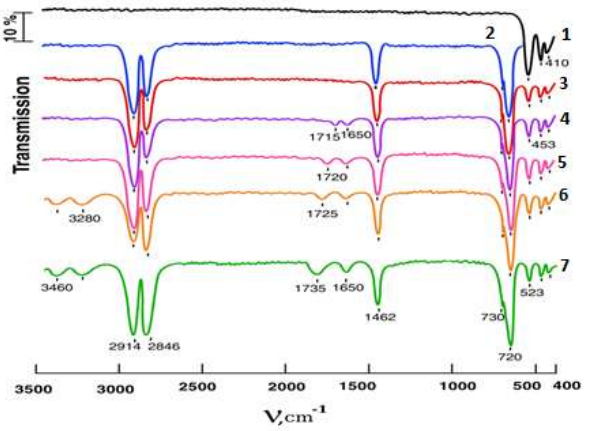


*Fig. 2. FTIR – spectra of initial and gamma irradiated HDPE/GaAs<Te> composite films: GaAs<Te> (1); HDPE (2); HDPE/ GaAs<Te (3); 50 (4); 150 (5); 250 (6), and 350 kGy (7)*

The peaks at 2914 and 2846 $cm^{-1}$ represent the antisymmetric and symmetric stretching of C-H bond in $–CH_2$-$CH_2$-chain; 1462 $cm^{-1}$ band represent bending vibration of C-H bond deformation in the plane; 730 $cm^{-1}$ represents inner rocking vibration of $–CH_2$- in the crystalline part and 720 $cm^{-1}$ as inner rocking vibration of $–CH_2$- in the amorphous part of HDPE [19]. The main observed transmission bands and their assignments are listed in Table 1.

Table 1

Main vibrations of initial and gamma irradiated HDPE films

| Wave number ν, $cm^{-1}$ | Initial | Dose, kGy | | | | | | | Functional group, types of vibration |
|---|---|---|---|---|---|---|---|---|---|
| | 0 | 50 | 100 | 150 | 200 | 250 | 300 | 350 | |
| 2914 | 2914 | 2914 | 2914 | 2914 | 2914 | 2914 | 2914 | 2914 | $\nu_{as}$ ($-CH_2$) stretching |
| 2846 | 2846 | 2846 | 2846 | 2846 | 2846 | 2846 | 2846 | 2846 | $\nu_s$ ($-CH_2$) stretching |
| – | – | 1715 | 1715 | 1715 | 1720 | 1725 | 1730 | 1735 | ν (–C=O–) stretching (carbonyl) |
| – | – | 1650 | 1650 | 1650 | 1650 | 1650 | 1650 | 1650 | ν –C=C–) stretching (polyene) |
| 1462 | 1462 | 1462 | 1462 | 1462 | 1462 | 1462 | 1462 | 1462 | δ ($CH_2$) deformation in the plane (amorphous phase) |
| 730 | 730 | 730 | 730 | 730 | 730 | 730 | 730 | 730 | δ ($CH_2$) Inner rocking of ($-CH_2$) crystal phase |
| 720 | 720 | 720 | 720 | 720 | 720 | 720 | 720 | 720 | δ ($CH_2$) Inner rocking of ($-CH_2$) amorphous phase |

Figs. 1 and 2 also show the transmission spectra of semiconductor filler GaAs<Te>. As observed, these spectra are characterized by the presence of phonon vibrations in the frequency range of ν = 600…400 $cm^{-1}$, with maxima at 523, 453, and 410 $cm^{-1}$. The stability of the intensities of these bands served as one of the main criteria for obtaining homogeneous composite films with same thickness (d = 100 μm) [17, 18].

It should be noted that in the gamma-irradiated samples of HDPE polymer and its composite (HDPE/GaAs<Te>) films, new bands appear in the transmission spectra in the frequency ranges ν = 1700…1750 and 1670…1580 $cm^{-1}$ (see Figs. 1 and 2). As follows from the figures, carbonyl groups (C=O) are formed in the range ν=1700…1750 $cm^{-1}$. Similar results have also been reported in other studies [15, 16], where the ν = 1720 $cm^{-1}$ band was mainly attributed to ketone groups. As the absorbed radiation dose increases from 50 to 350 kGy, the maximum of the carbonyl band shifts by 15 $cm^{-1}$ toward higher frequencies (ν = 1735 $cm^{-1}$), and its half-width ($\nu_{1/2}$) broadens by ~ 30 $cm^{-1}$. This indicates the formation of various

carbonyl-containing degradation products (carboxylic acids, aldehydes, and ketones) resulting from rearrangement and reconstruction of macromolecular radicals [11, 20].

The transmission bands in the frequency range of $\nu = 1670…1580$ cm$^{-1}$ correspond to stretching vibrations of –C=C-bonds, mainly associated with the formation of polyene groups. These bands exhibit a maximum at $\nu = 1650$ cm$^{-1}$ and a half-width $\nu_{1/2} = 35…60$ cm$^{-1}$ (see Figs. 1 and 2).

The formation of (–C=C–) and (C=O) groups under influence of γ-radiation in these composites is further confirmed by the appearance of optical absorption bands with maxima at wavelengths λ = 280 and 220 nm, respectively [5].

The transmission spectra of the (–C=C–) and (C=O) group bands in the frequency range of $\nu = 1700…1500$ cm$^{-1}$ were obtained under special recording conditions, enabling more accurate determination of their spectral parameters – such as peak positions, half-widths, and intensities (Fig. 3).

The optical densities of the (–C=C–) and (C=O) group bands were calculated using the following formula:

$$D = \lg(\frac{I}{I_0}), \quad (1)$$

where D, I, and $I_o$ are the optical density, the transmission and the incident intensities, respectively.

Table 2 presents the peak frequencies of the (–C=C–) and (C=O) group bands and their optical densities for HDPE and HDPE/GaAs<Te> films. As can be seen from the table, the maximum of the band (–C=C–) groups remains nearly unchanged as the absorbed dose increases from 50 to 350 kGy, while the optical density values increase.

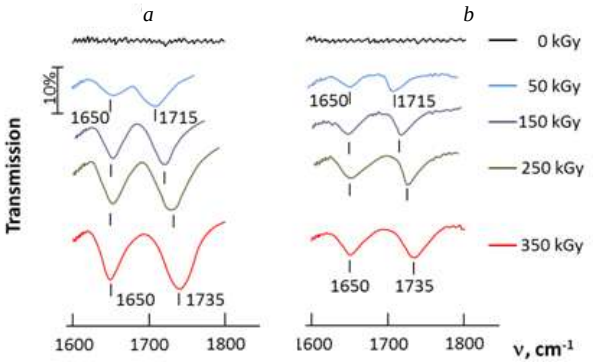


*Fig. 3. FTIR – spectra of (–C=C–) and (C=O) groups of initial and gamma irradiated HDPE polymer (1) and HDPE/GaAs<Te> (2) composite films in the frequency range ν = 1700…1500 cm$^{-1}$*

Table 2

Values of maxima and optical densities of carbonyl and polyene bands of gamma irradiated of HDPE polymer (1) and HDPE/GaAs<Te> (2) composite films

| No. | Sample | Wave number, cm$^{-1}$ | Dose, kGy | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 50 | 100 | 150 | 200 | 250 | 300 | 350 |
| | | | Optical density | | | | | | |
| 1 | HDPE | 1715…1735 | 0.16 | 0.20 | 0.22 | 0.22 | 0.22 | 0.21 | 0.20 |
| | | 1650 | 0.08 | 0.125 | 0.13 | 0.13 | 0.13 | 0.12 | 0.116 |
| 2 | HDPE/GaAs<Te> | 1715…1735 | 0.05 | 0.080 | 0.084 | 0.085 | 0.085 | 0.084 | 0.086 |
| | | 1650 | 0.024 | 0.041 | 0.042 | 0.042 | 0.042 | 0.042 | 0.043 |

In order to clarify the roles of crosslinking and chain scission processes in structural modifications affecting the radiation resistance of the investigated films, the dose dependencies of the optical density of the transmission band of (–C=C–) groups with a maximum of $\nu = 1650$ cm$^{-1}$ of HDPE polymer (curve 1) and HDPE/GaAs<Te> (curve 2) composite films were obtained (Fig. 4).

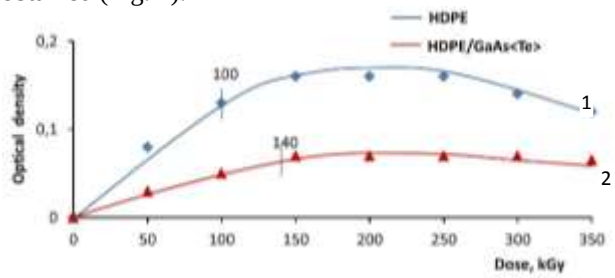


*Fig. 4. Dose dependences of the optical density of band at ν = 1650 cm$^{-1}$ of HDPE polymer and HDPE/GaAs<Te> composite films*

A comparative analysis of these dependencies revealed the following features:

1. All two curves are characterized by the presence of two regions: the first region at $\Phi_\gamma \leq 100…140$ kGy chain scission process; the second linear region at $100…140 \leq \Phi_\gamma \leq 300$ kGy is due to the chain scission process. The first region ($\Phi_\gamma \leq 100…140$ kGy) is dominated by the crosslinking process over chain scission. The second region ($100…140 \leq \Phi_\gamma \leq 300$ kGy) shows a linear increase in optical density, which is associated with the dominance of the chain scission process.

2. It is shown that the optical densities of the HDPE/GaAs<Te> composite films (1) are ~2 time lower, respectively, compared to the value of the HDPE polymer films. It is established that HDPE/GaAs<Te> composite films are more radiation-resistant in the absorbed dose range of $\Phi_\gamma = 50…350$ kGy than HDPE polymer films.

Comparative analysis of dose dependences of optical densities show that HDPE/GaAs<Te> composite films in the region of absorbed dose $\Phi_\gamma = 50…350$ kGy composite films are more radiation-resistant than HDPE films. The positive effect of the GaAs<Te> filler on the radiation resistance of the HDPE polymer matrix is also confirmed by a decrease in the optical densities of the carbonyl (C=O)-group band in the composite HDPE/GaAs<Te> films by ~ 1.5 times (see Table 2).

## 2.2. PHYSICAL STRUCTURAL MODIFICATION

As shown in Figs. 1 and 2, the FTIR transmission spectra of the initial HDPE polymer and HDPE/GaAs<Te> composite films exhibit absorption bands with maxima at 730 and 720 $cm^{-1}$. These bands correspond to the rocking vibrations of $CH_2$ groups in HDPE within the crystalline cell [19]. The absorption at 730 $cm^{-1}$ is characteristic of crystalline regions, while the band at 720 $cm^{-1}$ represents contributions from both crystalline and amorphous phases (see Table 1).

In the spectra of γ-irradiated polymer and composite films redistribution in the intensities of the 730 and 720 $cm^{-1}$ bands is observed, indicating physical structural changes in the irradiated samples. One of the key parameters characterizing these structural changes is the degree of crystallinity. The degree of crystallinity of the samples was calculated based on the optical densities using the following formula [19]:

$$K = \frac{1.4\cdot(D_{730}/D_{720})}{1+0.4(D_{730}/D_{720})}, \qquad (2)$$

where $D_{730}$ and $D_{720}$ are optical density of 730 and 720 $cm^{-1}$ bands, respectively, in the FTIR spectra for HDPE polymer and HDPE/GaAs<Te> composite films.

The relative degrees of crystallinity ($K_\gamma/K_0$) were determined for both the initial and irradiated HDPE polymer and HDPE/GaAs<Te> composite films.

The dose dependences of the relative degree of crystallinity $K_\gamma/K_0$ in the absorbed dose range $\Phi_\gamma = 50…350$ kGy for HDPE polymer and HDPE/GaAs<Te> composite films are shown in Fig. 5.

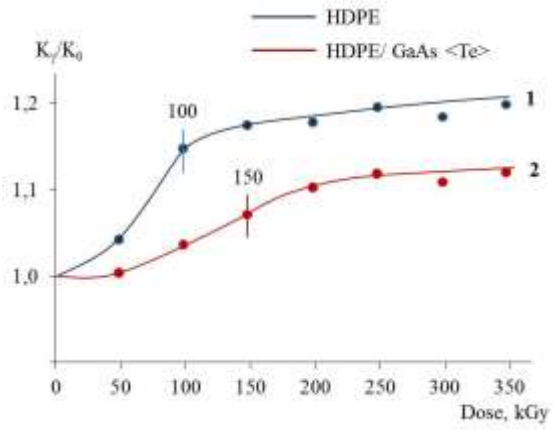


*Fig. 5. Dose dependences of the relative degree of crystallinity $K_\gamma/K_o$ for HDPE polymer and HDPE/GaAs<Te> composite films*

As can be seen from the Fig. 4 the dose dependences for both polymer and composite films consists of linear and stationary regions. In the linear region, the rate of change of $K_\gamma/K_0$ values for HDPE polymers is ~ 2.6 times higher than for HDPE/GaAs<Te> composites (curve 2). At values $100 \le \Phi_\gamma \le 350$ kGy and $150 \le \Phi_\gamma \le 350$ kGy the $K_\gamma/K_0 = f(\Phi_\gamma)$ curves reach saturation, respectively. Comparison of dose dependences indicates that HDPE/GaAs<Te> composite film is more radiation-resistant than HDPE polymer.

The observed features are associated with the formation of radiation defects in the HDPE matrix and a change in the interaction at the interface. Due to changes in the interfacial interaction, the supramolecular structure (SMS) of the polymer changes [19]. The active centers created in the HDPE matrix after gamma irradiation interact with the surface of gallium arsenide micro particles doped with tellurium (GaAs<Te>), which leads to a change in the degree of crystallinity and accordingly, the structure. A comparative analysis of the dose dependencies of crystallinity (representing physical structural modification) and the optical density of the C=O stretching band (representing chemical structural modification) reveals the following:

1. The dose dependencies for both physical and chemical structural modifications exhibit a similar trend. In both cases, they are characterized by the presence of two regions – linear and stationary.

2. A correlation was observed between physical and chemical structural modifications of the polymer and its composite, indicating a direct relationship between the degree of crystallinity and the crosslinking process.

3. The investigated HDPE/GaAs<Te> composite films were found to be more radiation-resistant than the HDPE polymer films.

## CONCLUSIONS

Physical and chemical structural modifications in HDPE polymer and HDPE/GaAs<Te> composite films induced by gamma irradiation in the absorbed dose range $\Phi_\gamma = 50…350$ kGy at room temperature in air were investigated by the method of Fourier-IR spectroscopy. Dose dependencies of the degrees of crystallinity (representing physical modification) and the optical densities of the characteristic polyene (–C=C–) and carbonyl (C=O) functional group bands (representing chemical modification) were obtained and their features were analyzed. It was shown that the dose dependencies for both physical and chemical structural modifications exhibit a similar trend. In both cases, they are characterized by the presence of two regions – linear and stationary. A correlation between radiation-induced physical and chemical structural modifications of the polymer and its composite films has been identified, indicating a relationship between the degree of crystallinity and the crosslinking process. Comparative analysis confirms that in the $\Phi_\gamma = 50…350$ kGy absorbed dose range HDPE/GaAs<Te> composite films are more radiation-resistant than HDPE polymer films. This effect is attributed to alterations in the supramolecular structure of the films and differences in the interfacial interactions between the polymer matrix and the fillers. In the case of the composite films, these interactions result in a more stable matrix structure, thereby enhancing their radiation resistance.

## REFERENCES

1. M.I. Aliev, N.N. Gadzhieva, G.B. Ahmadova. Fourier-IR study of the high-density polyethylene composites with semiconductor fillers GaAs and GaAs *// International Journal of Composite Materials*. 2014, N 1, p. 1-3.

2. M.I. Aliev, N.N. Gadzhieva, G.B. Akhmedova. A Fourier Transform Raman Spectroscopic Study of the Structures of Polyethylene Composite Films Containing

GaAs and GaAs<Te> // *Polymer Science. Series A.* 2016, v. 58, N 3, p. 438-442.

3. N.N. Gadzhieva, G.B. Ahmadova. Effect of γ-irradiation on the structure of high-density polyethylene composites with GaAs and GaAs<Te> fillers // *Problems of Atomic Science and Technology*. 2020, N 4(128), p. 28-30.

4. N.N. Gadzhieva, G.B. Ahmadova, S.Z. Melikova, F.G. Asadov. X-ray diffractometric study of HDPE/GaAs and HDPE/GaAs<Te> composites // *Physics and Chemistry of Solid State.* 2023, v. 24, N 1, p. 23-25.

5. N.N. Gadzhieva, G.B. Akhmedova, R.A. Mammadov. Structures of HDPE/GaAs and HDPE/GaAs<Te> Composites Irradiated with gamma quanta // *Problems of Atomic Science and Technology*. 2024, N 4(152), p. 20-22.

6. N.N. Gadzhieva, G.B. Akhmedova. Radiation effects in semiconductor composites HDPE/GaAs and HDPE/GaAs<Te> // *Journal of Radiation Researches*. 2020, v. 7, N 1, p. 35-40.

7. N.N. Gadzhieva, G.B. Akhmedova, R.A. Mammadov, G.I. Muradova. Spectroscopy study of structures of HDPE polymer and HDPE/GaAs composite films irradiated with gamma quanta // *Journal of Radiation Researches.* 2024, v. 11, N 2, p. 42-47.

8. A.N. Nabiyeva. Investigation on the effect of γ-radiation on the dielectric properties of HDPE/α-$Al_2O_3$ nanocomposites // *Transactions of ANAS*. 2022, XVII, N 5, p. 116-122.

9. A.A. Nabiyev, A. Oleyniczak, A. Pawlukajc, et al. Nano-ZrO: filled high-density polyethylene composites: structure, thermal properties, and the influence of γ-irradiation // *Polymer Degradation and Stability*. 2020, v. 171, p. 109042.

10. Sh.G. Prasad, Ch.Z. Ranjan Sahu, A. Saha, U. De. Spectroscopic Investigation of Degradation Reaction Mechanism in γ-Rays Irradiation of HDPE // *Biointerface Research in Applied Chemistry*. 2021, v. 11, N 2, p. 9405-9419.

11. I.I. Mustafayev, S.Z. Melikova, E.G. Hajiyeva, et al. Spectral investigations of γ-irradiated polyethylene/CdS+ZnS composite films // *Acta Physica Polonica A.* 2023, v. 144, N 1, p. 35-37.

12. D.E. Abulyazied, E.F.M. El-Zaidia. Nanoindentation and optical properties of high-density polyethylene/ZnO nanoparticles composites // *Journal of Ovonic Research.* 2018, v. 14, N 5, p. 359-370.

13. I.I. Mustafayev, S.Z. Melikova, E.G. Hajiyeva, et al. Spectral investigations of γ-irradiated polyethylene/CdS+ZnS composite films // *Acta Physica Polonica A.* 2023, v. 144, N 1, p. 35-37.

14. R.K. Dhillion, P. Singh, S.K. Gupta, et al. Study of high energy (MeV) $N^{6+}$ ion and gamma radiation induced modifications in low-density polyethylene (LDPE) polymer *// Nuclear Instruments and Methods in Physics Research B.* 2013, v. 301, p. 12-16.

15. A.A. Moez, S.S. Aly, Y.H. Elshaer. Effect of gamma radiation on low-density polyethylene (LDPE) films: optical, dielectric and FTIR studies // *Spectrochimica Acta Part A – Molecular and Biomolecular Spectroscopy*. 2012, v. 93, p. 203-207.

16. S.K. Raghuvanshi, B. Ahmad, A.K. Srivastava, et al. Effect of gamma irradiation on the optical properties of UHMWPE polymer // *Nuclear Instruments and Methods in Physics Research B.* 2012, v. 271, p. 44-47.

17. A.H. Kuptsov, G.N. Zhizhin. *Handbook of Fourier Transform Raman and Infrared Spectra of Polymers.* M.: *"*Fizmatlit*"*, 2001, p. 2-3.

18. B.A. Kolesov. *Applied Raman Spectroscopy*. Novosibirsk: *"*SORAN*"*, 2018, p. 46-48.

19. A.M. Magerramov. *Structural and radiation modified electret, piezoelectric properties of polymer composites.* Baku: *"*Elm*"*, 2001, p. 87-89.

20. D. Sinha. Structural modifications of gamma irradiated polymers: an FT-IR study // *Advances in Applied Science Research.* 2012, v. 3, N 13, p. 1365-1371.

*Article received 01.07.2025*

## СТРУКТУРНІ МОДИФІКАЦІЇ ПОЛІМЕРУ ПЄВП ТА КОМПОЗИТНИХ ПЛІВОК ПЄВП/GaAs<Te>, ЯКІ ІНДУКОВАНІ ГАММА-ОПРОМІНЕННЯМ

***Н.Н. Гаджієва, Г.Б. Ахмедова, Р.А. Маммадов***

Представлено результати дослідження фізичних та хімічних структурних модифікацій, викликаних гамма-опроміненням у полімерних плівках ПЄВП та композитних плівках ПЄВП/GaAs<Te> у діапазоні поглинених доз $\Phi_\gamma$ = 50…350 кГр. Показано, що гамма-опромінення викликає зміни ступеня кристалічності та утворення полієнових (–C=C–) та карбонільних (C=O) груп у полімерних та композитних плівках. Дозові залежності для цих модифікацій демонструють подібну тенденцію, що вказує на прямий зв'язок між ступенем кристалічності та процесом зшивання. Порівняльний аналіз підтверджує, що композитні плівки є більш радіаційно стійкими, ніж полімерні плівки.