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SPECTROSCOPIC STUDY OF STRUCTURES OF HDPE POLYMER AND HDPE/GaAs COMPOSITE FILMS IRRADIATED WITH GAMMA QUANTA

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Abstract: This study presents the results of optical (UV-Vis) and Fourier Transform Infrared (FTIR) spectroscopy analyses of structural changes in HDPE polymer and HDPE/GaAs composite films irradiated with gamma quanta at doses of 100, 200, and 300 kGy at room temperature. Gamma irradiation of the initial polymer and its composite films was found to induce the formation of optical absorption bands at 220 and 280 nm, as well as FTIR transmission bands at v = 1650 and 1715–1735 cm⁻¹, indicating the presence of C=O (carbonyl) and C=C (polyene) groups. It was established that HDPE/GaAs composite films exhibit greater radiation resistance than HDPE polymer in the absorbed dose range of 100–300 kGy.

Keywords: composite, gamma radiation, absorbance, transmission.

1. Introduction

Polymer composite materials such as polymer-semiconductor fillers are of special interest. The introduction of new fillers typically enhances the practical applicability of composite materials. The addition of semiconducting fillers into the polymer matrix leads to changes in its structure and properties. From this perspective, it is important to study composites based on high-density polyethylene (HDPE) and gallium arsenide (GaAs) semiconductor compounds. Using these materials as modifying additives for polymers can lead to the production of new composites with different electro physical, dielectric, thermal, optical luminescent and mechanical properties. It is important to note that there is a lack of sufficient scientific information on the study of these composites in the literature [1–6].

Currently, radiation technologies are widely employed to enhance the physical and chemical properties of polymers and their composite materials in high-tech applications. Ionizing radiation leads to irreversible physical and chemical changes in the structure of these materials at the macromolecular level. Obtaining a comprehensive dataset on the structural changes and properties of polymer-semiconductor composite systems under the influence of ionizing gamma radiation will facilitate the development and production of multifunctional composites. This will enable the development and production of new polymer composite materials with tailored properties for electronic devices and systems, as well as the creation of specialized electrical insulation systems and high-voltage technologies. These materials also allow for effective radiation devices, and the instrument panels of special devices operating in a high-radiation background.

The fact that HDPE is taken as a matrix is due to its extensive study. The use of GaAs semiconductor as a filler is due to its unique structure. In addition, GaAs exhibits radiation resistance.

The investigations of structural changes, optical, and electrophysical properties of HDPE/GaAs composite films were studied as a function of filler concentration. However, the structural changes in this composite due to the gamma radiation have not been sufficiently studied. Therefore, this paper presents the results of optical and FTIR studies on the structural changes in HDPE/GaAs composite irradiated with gamma radiation.

2. Technique of experiments

High-density polyethylene (PE 2 NT11-285D, Russia, Kazan), with a melting point of 130 °C and a density of 947 kg/m³, was selected as the polymer matrix. GaAs semiconductor was used as the filler. HDPE and HDPE/GaAs films were obtained using the high pressing method [3, 6].

HDPE and HDPE/GaAs films with a thickness of approximately 100 μ m were irradiated with gamma radiation using an MRX- γ -20 (⁶⁰Co) gamma device, with an exposure rate of $d\Phi/dt = 1.06$ Gy/s. The samples were irradiated at doses of 100, 200, and 300 kGy at room temperature.

The optical absorption spectra of these films were measured using a UV-VIS spectrophotometer (Varian Cary 50 Scan) in the wavelength range of $\lambda = 200-800$ nm. The spectra were obtained for the absorbance of the polymers and composites as a function of wavenumber.

Fourier-transform infrared (FTIR) transmission spectra of these films were recorded using a Varian 640 FTIR spectrometer at room temperature in the v = 4000-400 cm⁻¹ frequency range. The spectra were obtained for the polymers and composites as a function of wavenumber.

The variation before and after irradiation was compared, and peak analysis was performed to study the changes in the position and relative intensity of the bands.

3. Results and discussion

Figures 1 and 2 show the optical (UV-VIS) absorption spectra of initial (unirradiated) and gamma-irradiated HDPE polymer and HDPE/4 mass % GaAs composite. The choice of the mass content of micro particles (4 mass %) of GaAs is based on the fact that at this content, the degree of crystallinity has a value of K = 70 % [1, 2, 5].

From figures 1 and 2 clearly show that the unirradiated HDPE polymer and its composites do not exhibit absorption bands in the studied wavelength range ($\lambda = 200-800$ nm). On the other hand, the spectra of irradiated HDPE polymer (Fig.1) and HDPE/GaAs composite films exhibit a shoulder band in ~220 nm. This band is attributed to the C=O group in the molecular macromolecule (carbonyl). This indicates that the band gap width decreases with irradiation, while the absorption coefficient increases with irradiation [5, 7–10].



Fig. 1. Absorption spectra of the initial and gamma-irradiated HDPE polymer (a) and HDPE/GaAs composite (b) films.

It should be noted that the absorption band shifts towards longer wavelengths with an increasing gamma irradiation dose. Gamma irradiation induced the cleavage of C–C bonds and the dehydrogenation of polymeric chains (i.e. the escape of hydrogen atoms), leading to the formation of conjugated -C=C- bonds ($\lambda = 280$ nm). The increase in the number of conjugated -C=C- bonds with increasing gamma irradiation dose results in a shift of the absorption band towards longer wavelengths. The behavior is generally interpreted as being caused by the formation of extended systems of conjugated bonds, i.e., the possible formation of carbon clusters [1, 5, 10–15]. The absorption bands in ~ 280 nm are associated with the electronic $\pi \rightarrow \pi^*$ transitions occurring in the unsaturated centers of the molecules, i.e., in compounds containing double or triple bands, as well as in aromatics. The excitation of π -electron requires less energy; hence, transition of this type occur at longer wavelengths.

We have obtained dose dependences of the intensities of the optical absorption bands C=O in HDPE polymer (1) and HDPE/GaAs composite (2) films (Fig. 2).



Fig. 2. Dose dependence of the intensity of optical absorption band at $\lambda = 280$ nm. 1 - HDPE and 2 - HDPE/GaAs.

For HDPE polymer and HDPE/GaAs composite films irradiated with 1.2 MeV gamma rays, new bands were detected at 1650 and 1715–1735 cm⁻¹, attributed to the formation of -C=C- (polyene) and polymer oxidation, and the formation of (carbonyl) C=O groups [1, 3, 5, 16–20]. The formation of C=O (carbonyl) and C=C (polyene) groups in the Fourier-IR transmission spectra is also confirmed by the appearance of transmission bands with maxima at v = 1715–1735 cm⁻¹ and v = 1630 cm⁻¹, respectively (Fig. 3a and 3b).



Fig. 3. FTIR transmission spectra of HDPE polymer (a) and HDPE/GaAs (b) composite films, irradiated with gamma absorption doses of 100, 200, 300 kGy, in frequency range v = 1600-1800 cm⁻¹.

As seen in Figures 3a and 3b, increasing the gamma irradiation dose in both samples leads to a redistribution of C=O and C=C groups. At the same time, the position of the C=C band remains unchanged ($v = 1650 \text{ cm}^{-1}$); however, the maximum of the C=O band shifts toward higher

frequencies by $\Delta v = 20 \text{ cm}^{-1}$ (from 1715 to 1735 cm⁻¹). The observed shift apparently indicates the formation of decomposition products of various carbonyl groups (such as carboxylic acids, aldehydes, and ketones) resulting from the rearrangement and reconstruction of macromolecular radicals [5, 16, 20–24]. Analysis of the intensities of these bands as a function of gamma irradiation dose indicates that, in the absorbed dose range of 100–300 kGy, the HDPE/GaAs composite exhibits higher radiation resistance than HDPE.

4. Conclusion

For the first time, structural changes caused by the influence of gamma irradiation of initial HDPE and HDPE/GaAs composite films at doses of 100, 200, and 300 kGy at room temperature were studied. It has been shown that gamma irradiation of these composites leads to the formation of optical absorption bands at 220 and 280 nm. These absorption bands belong to C=O and -C=C-groups. The formation of C=O (carbonyl) and C=C (polyene) groups in the Fourier-IR transmission spectra is also confirmed by the appearance of transmission bands with maxima at v = 1715-1735 cm⁻¹ and v = 1630 cm⁻¹, respectively. Analysis of the intensities of optical and FTIR bands as a function of the gamma irradiation dose indicates that, in the absorbed dose range of 100–300 kGy, the HDPE/GaAs composite films exhibit higher radiation resistance than HDPE polymer films.

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СПЕКТРОСКОПИЧЕСКОЕ ИССЛЕДОВАНИЕ СТРУКТУРЫ ПОЛИМЕРА ПЭВП И КОМПОЗИТНЫХ ПЛЁНОК ПЭВП/GaAs, ОБЛУЧЕННЫХ ГАММА-КВАНТАМИ

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Резюме: Представлены результаты оптических (УФ-видимая спектроскопия) и Фурье-ИКспектроскопия, структурных изменений в полимере ПЭВП (полиэтилен высокой плотности) и композитных пленках ПЭВП/GaAs, облучённых гамма-квантами при дозах 100, 200 и 300 кГр при комнатной температуре. Установлено, что гамма-облучение исходного полимера и композитных пленок приводит к формированию полос оптического поглощения при 220 и 280 нм и полос пропускания в ИК-области при v = 1650 и 1715–1735 см⁻¹, что свидетельствует о формировании карбонильных (C=O) и полиеновых (C=C) групп. Установлено, что композитные пленки ПЭВП/GaAs обладают наибольшей радиационной стойкостью в диапазоне поглощённых доз 100–300 кГр по сравнению с полимером ПЭВП.

Ключевые слова: композит, гамма-излучение, поглощение, пропускание.

QAMMA KVANTLARI İLƏ ŞÜALANMIŞ YSPE VƏ YSPE/GaAs KOMPOZİT NAZİK TƏBƏQƏLƏRİNİN QURULUŞUNUN SPEKTROSKOPİK TƏDQİQİ

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Xülasə: Bu işdə otaq temperaturunda 100, 200 və 300 kQr dozalarda qamma kvantları ilə şüalanan YSPE polimer və YSPE/GaAs nazik təbəqələrində baş verən quruluş dəyişikliklərinin optik (UV VIS) və Furye İQ (FTİR) tədqiqatlarının nəticələri təqdim olunur.. Müəyyən edilmişdir ki, ilkin polimer və onun kompozit nazik təbəqələrinin qamma şüalanması nəticəsində 220 və 280 nm dalğa uzunluqlarında optik udulma zolaqları, eləcə də v = 1650 və 1715–1735 sm⁻¹-də FTİR buraxma zolaqlarının əmələ gəlir ki, bu da karbonil (C=O) və polien (C=C) qruplarının formalaşmasını göstərir. Tədqiqat nəticələri göstərmişdir ki, 100–300 kQr intervalında YSPE/GaAs kompozit nazik təbəqələri YSPE polimerinə nisbətən daha yüksək radiasiya davamlılığa malikdir.

Açar sözlər: kompozit, qamma şüalanma, udulma, buraxma.