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IR SPECTRA OF γ-IRRADIATED NANOCOMPOSITES ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE / α-SiO_2

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The effect on concentration of the nanofiller α-SiO_2 filler and irradiation on the FTIR spectra of pure films polymer (ultra-high molecular weight polyethylene (UHMWPE)) and doped them this α-SiO_2 with different concentration (0, 1, 3, 5 vol.%) were investigated using FTIR technique. The samples were irradiated for different doses like 0, 50, and 100 kGy by ^{60}Co source with a dose rate of approximately $3.3 \cdot 10^{-3}$ kGy/h at room temperature. The correlation of absorption bands with occurrence of corresponding groups was carried out. The occurrence of a series of a characteristic absorptions bands of composites was shown.

INTRODUCTION

Polymer composite materials (PCM) have a set of properties that allow them to be used as high-voltage electrical insulating materials at nuclear power plants and reactors, in power supply systems for satellites and spacecraft [1–3] of outer coatings of spacecraft [4], where nuclear radiation is always present. However, during operation, the negative factors of outer space significantly worsen the initial characteristics of materials. In this regard, when developing new composite materials (CM), special attention should be paid to the radiation-induced behavior of CM properties and it is necessary to assess the degree of impact of negative factors of outer space. The degree of these changes for each material depends on many factors: the initial structure, the composition of the material, the degree of its purity, the characteristics of the incident radiation, the radiation dose, etc. [5]. The impact of radiation on PCMs leads to a change in their defect structure and, as a consequence, in physical and chemical properties. In this case, one of the main tasks of researchers is to establish the nature of the creation and evolution of a defect structure, the relationship between radiation-induced defectiveness with changes in the properties of materials. Radiation exposure leads to a significant change in the structure of materials. There is a spatial transformation of the material, the entire molecular macromolecule changes, as well as the accumulation of some and the disappearance of other types of chemical bonds, etc. All these structural changes have a significant effect on the rearrangement of the superamolecular structure and, as a result, on the variety of properties of the PCM [6].

Composites based on ultra-high molecular weight polyethylene (UHMWPE) stand out among the CM, which are currently receiving close attention, and it is assumed that for CMs used in the space industry, UHMWPE, which belongs to a new generation of polymers with unique physical and mechanical properties, is one of the most promising matrix, and composites based on it can meet the requirements for materials intended for this industry [6–14].

In the UHMWPE composite system, a wide modification of the properties is possible by changing the ratio of the components or introducing different fillers.

The aim of this work is to show the effect of γ-irradiation and nanoscale α-SiO_2 on the IR spectra of UHMWPE and composites based on it.

EXPERIMENTAL PART

Powdered UHMWPE with an average molecular weight of $1.55 \cdot 10^6$, a degree of crystallinity of 65%, a melting point of 190 °C and a density of 940 kg/m^3 was used as a polymer matrix, temperature of transition to the plastic state 138…142 °C. The filler was a powder of amorphous silicon dioxide α-SiO_2 (Sky Spring Nanomaterials, Inc. Hauston, USA) with a spherical particle size $d = 20$ nm, a specific surface area $S = 160$ m^2/g and a density of 2.65 g/cm^3 [9].

In the manufacture of film samples, the following technological scheme was used:

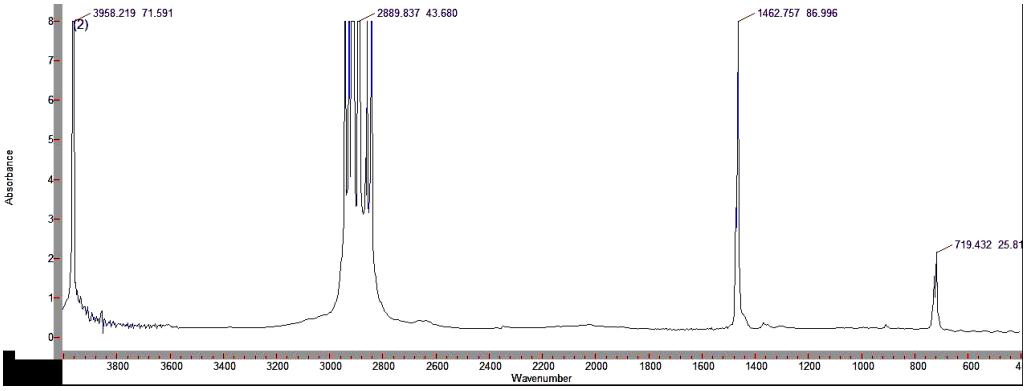
– mixing UHMWPE and α-SiO_2 powders in a porclain mortar;

– pressing a homogeneous mixture of powder components in a hydraulic press with heated plates at a pressure of 15 MPa with holding at a temperature of 190 °C for 5 min and obtaining composite samples in the form of disks with a diameter of 20 mm and a thickness of 50…80 μm.

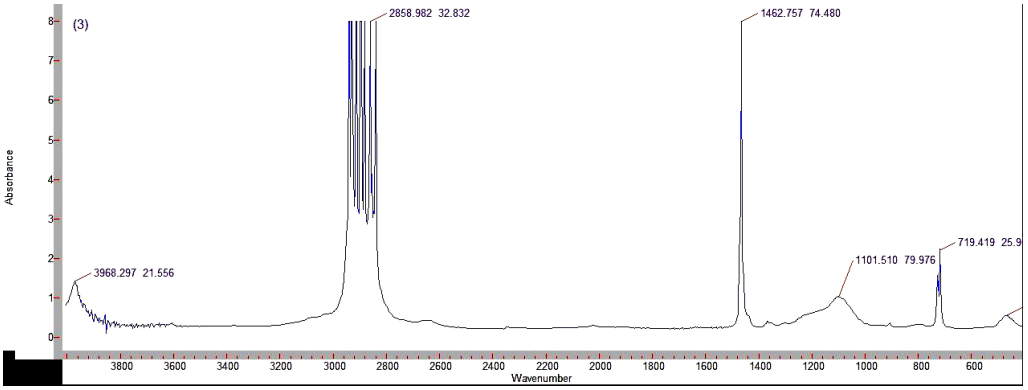
– to ensure reliable electrical contact between the sample and stainless steel electrodes by pressing onto both surfaces of the samples an electrode made of thin aluminum foil 7 μm thick, followed by cooling in a water – ice mixture (quenching mode).

Samples of the polymer composite material were a polymer film with different volumetric concentrations (Φ) of the filler: 1, 3, and 5%. Pure UHMWPE was taken as a control sample.

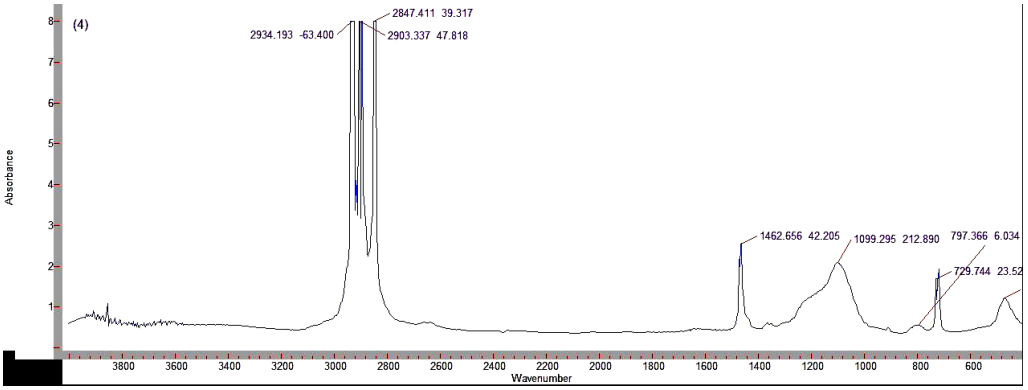
Studies of the effect of filler concentration and of gamma-irradiation included measurements of the IR spectrum of pure UHMWPE films and PCM based on it before and after exposure to these factors.



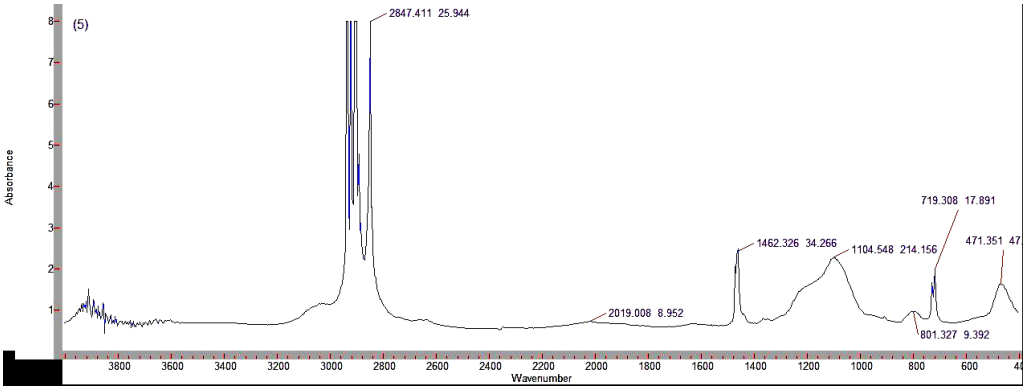
IYMPE-initial, 72 μm *a*



IYMPE+1%SiO_2, 69 μm *b*

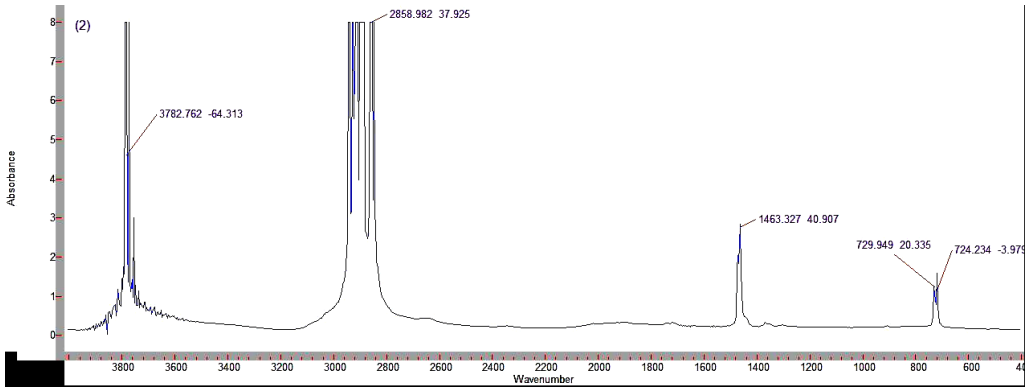


IYMPE+3%SiO_2, 75 μm *c*

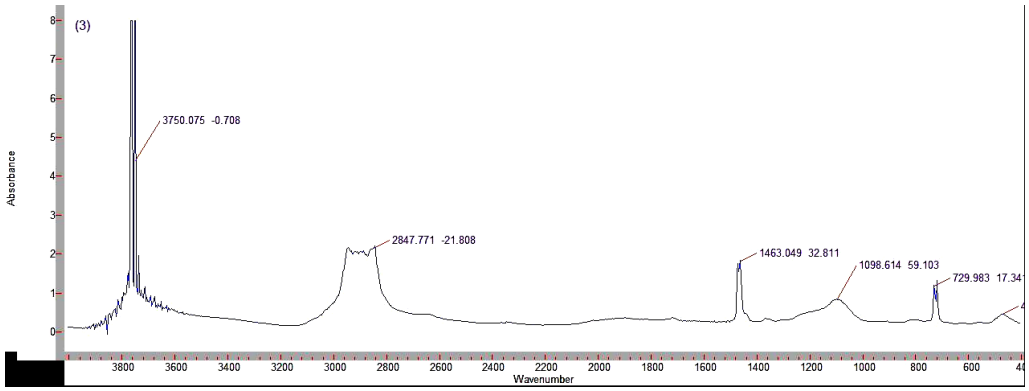


IYMPE+5%α- SiO_2, 65…70 μm *d*

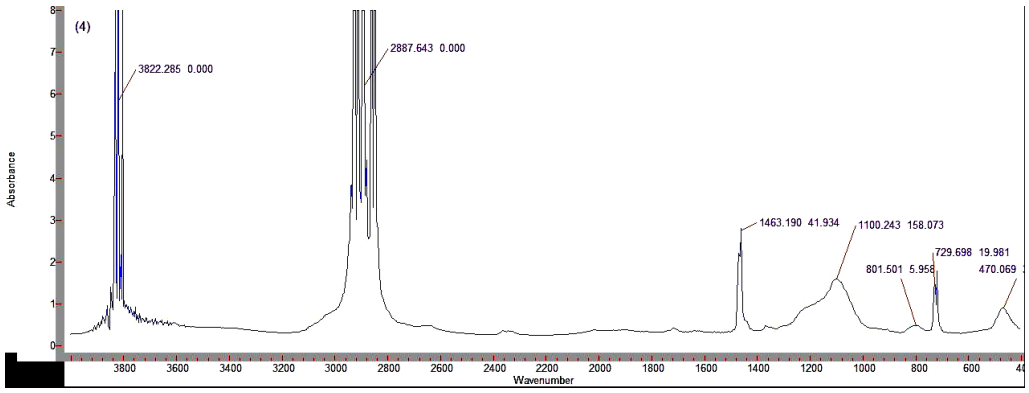
Fig. 1. IR absorption spectra of pure UHMWPE (a) and composites based on it: b – 1; c – 3; d – 5%; α-SiO_2



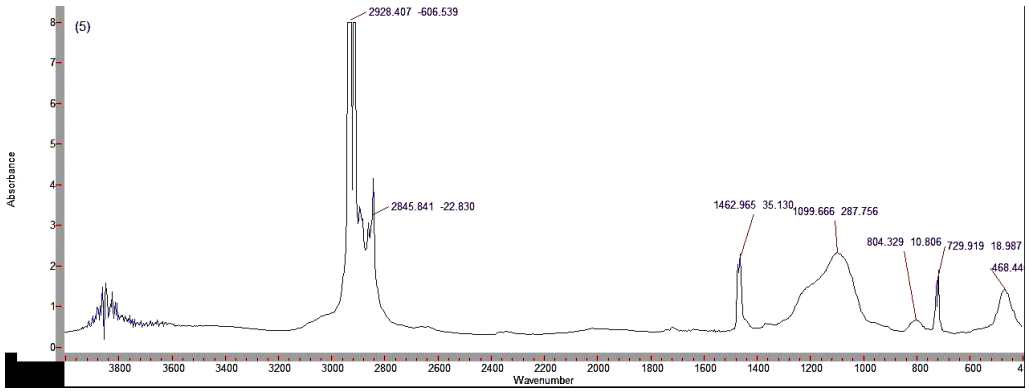
IYMPE-initial, h=58 μm *a*



IYMPE+1%SiO_2, h=55 μm *b*

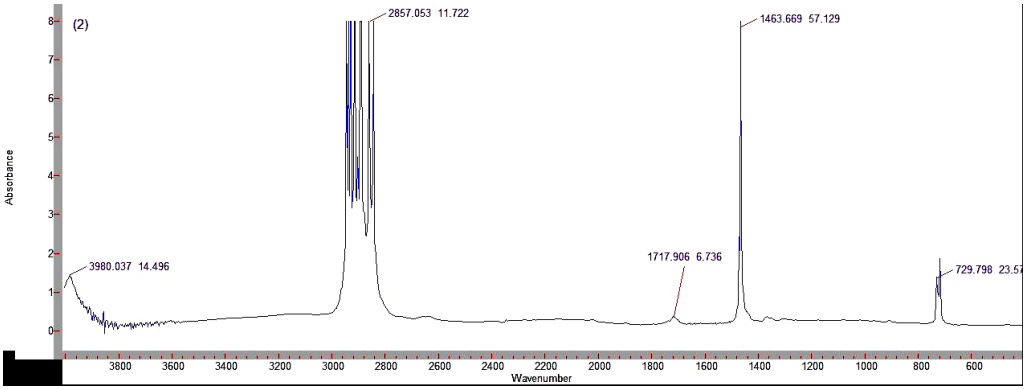


IYMPE+3%SiO_2, h=61 μm *c*

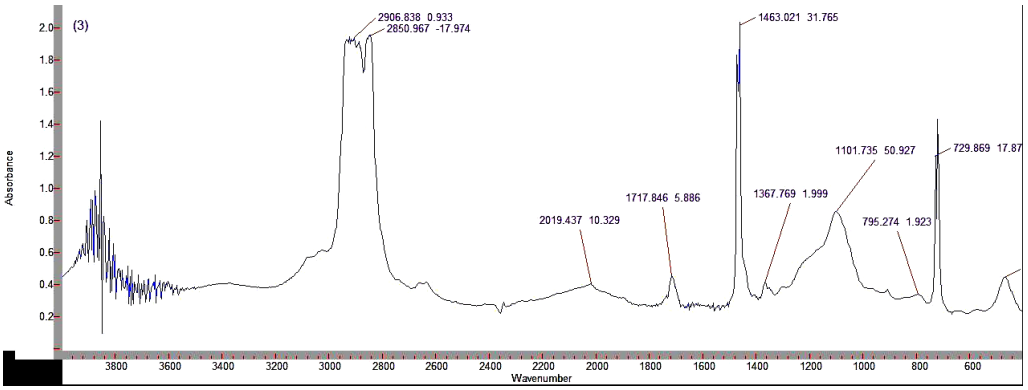


IYMPE+5%SiO_2, h=57 μm *d*

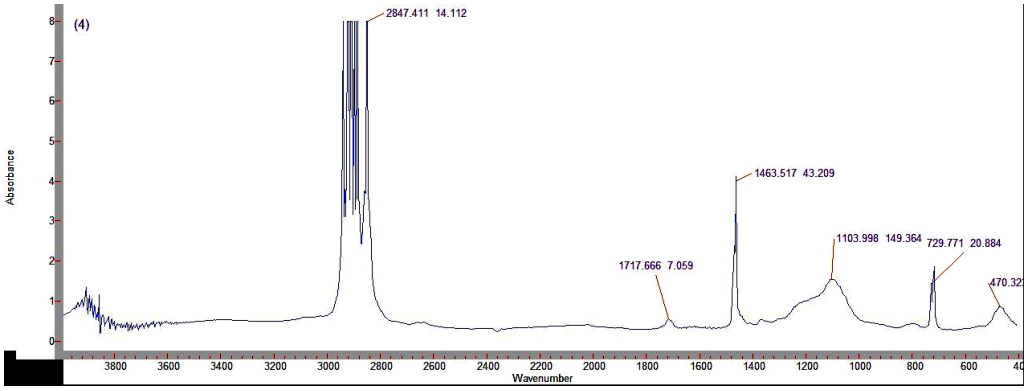
Fig. 2. IR spectra for UHMWPE (a) and UHMWPE with nanocomposite additives α-SiO_2 from irradiated dose of 50 kGy: b – 1; c – 3; d – 5%



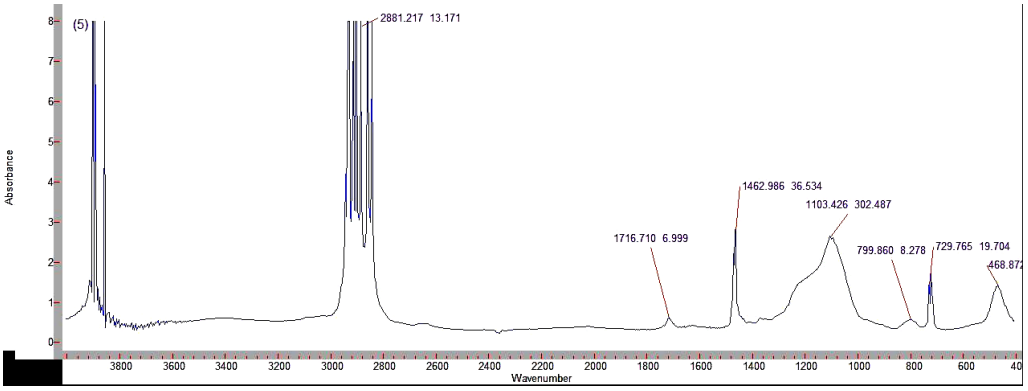
IYMPE-initial, h=58 μm *a*



IYMPE+1%SiO_2, h=55 μm *b*



IYMPE+3%SiO_2, h=61 μm *c*



IYMPE+5%SiO_2, h=57 μm *d*

Fig. 3. IR spectra for UHMWPE (a) and UHMWPE with nanocompositions with α-SiO_2 additives from irradiated with a dose of 100 kGy: b – 1; c – 3; d – 5%

The samples were irradiated on an MRX-γ-20 (^{60}Co) gamma-device, with which the exposure dose rate of the γ-radiation source was $3.3 \cdot 10^{-3}$/h UHMWPE film and composite samples were irradiated to absorbed doses D = 50 and 100 kGy.

Spectral studies were performed on a Varian 640-IRFT Fourier spectrometer in the range 4000…400 cm^{-1}.

RESULTS AND DISCUSSION

Analysis of the IR spectra of the samples (Fig. 1) of both the initial unirradiated UHMWPE and the composites based on, indicates the presence and coincidence of all the main peaks for the characteristic frequencies of the 3958, 2889 cm^{-1} band, which is responsible for the symmetric stretching vibrations of CH bonds, a doublet in the region of 1472…1462 cm^{-1}, due to deformation vibrations of CH_2-groups, as well as pendulum vibrations of groups – CH_2-groups (doublet at 730…719 cm^{-1}, crystallinity bands). It can be seen from Fig. 1,b,c,d that the introduction of nanosized α-SiO_2 into UHMWPE up to 5 vol.% significantly changes the IR spectrum of pure UHMWPE. The most significant changes are observed in the 420…1600 cm^{-1} range. New bands appear in the IR spectra in the range of 471, 800 cm^{-1} (only for composites with α-SiO_2 concentration of 3 and 5 vol.%), 1100 cm^{-1}, the intensity of which increases with increasing α-SiO_2 concentration. The spectral line 471 cm^{-1} corresponds to the region of the boundary layer of the filler and the matrix [5]. In the opinion of the authors [10], some increase in the intensity of the C–O–C line in the range of 1100 cm^{-1} can be explained by the rupture of hydrocarbon chains of UHMWPE macromolecules with the formation of –OH and C–O bonds. In addition, there is a sharp decrease in the intensity of the absorption bands at 1462 and 3958 cm^{-1}, respectively.

Figs. 2 and 3 show the IR spectra of pure UHMWPE and nanocomposites based on it with different volumetric contents of α-SiO_2, irradiated with a dose of 50 and 100 kGy, respectively. And in the case of irradiated samples with an increase in the volume content of α-SiO_2 to 5 vol.%, a similar dependence of the peak intensity of the bands at 471 and 1100 cm^{-1} is observed, the maximum increase in the peak intensity is observed for samples of UHMWPE + 5% α-SiO_2 composites. With an increase in the absorbed dose up to 100 kGy, absorption bands in the 800 cm^{-1} range also appear for the UHMWPE + 1% α-SiO_2 composite. In addition, only in of UHMWPE + 1% α-SiO_2 the spectra composites irradiated with 100 kGy, dose two bands are observed: characteristic for alkenes at 1367 and 2020 cm^{-1}. The formation of a double bond indicates that, as a result of ionizing action, cross-linked structures are formed in the composite structure. The maximum increase in the peak intensity of the 1717 cm^{-1} band, found for all samples irradiated with a dose of 100 kGy, indicates the formation of bonds in ketones [11]. According to [15], the band appearing at 1717 cm^{-1} corresponds to > C = O stretching vibrations and the intensity of the peak increases in samples exposed to a higher dose of radiation. It is known that UHMWPE belongs to materials in which exposure to radiation leads to crosslinking of molecules. However, as can be seen from Fig. 3, the intensities of the peak of the 1717 cm^{-1} band of UHMWPE + 1% α-SiO_2 composites are relatively higher than those of other samples. This fact indicates a low oxidative destruction of UHMWPE. In addition to all that has been said, the following changes in the IR spectra of the irradiated samples should be noted:

– the absorbed dose of 50 kGy insignificantly affects the amplitude of the 1462 cm^{-1} band;

– the peak intensity of the absorption band at 2858 cm^{-1} for samples of nanocomposites of UHMWPE + 1% α-SiO_2 and 3782 cm^{-1} for samples of UHMWPE + 5% α-SiO_2 sharply decreases;

– in the spectrum of UHMWPE + 5% α-SiO_2 in the range of 2800…300 cm^{-1} a doublet appears at 2845…2928 cm^{-1};

– a doublet is observed on the spectra of UHMWPE + 1% α-SiO_2 samples irradiated with a dose of 100 kGy at 2850…2906 cm^{-1}. Thus, the analysis of the IR spectra of the samples of both the initial unirradiated UHMWPE and nanocomposites based on it indicates the presence and coincidence of all the main peaks for the characteristic frequencies. We assume that the results of this work, together with previously published data and other authors [6–17], should be used in the preparation of polymer nanocomposites based on crystallizing thermoplastics and exposure to γ-irradiation.

CONCLUSIONS

1. A characteristic feature of the IR spectrum of UHMWPE + α-SiO_2, not exposed to γ-radiation, is the appearance of absorption bands at 1100 and 471 cm^{-1}, which are associated with the breaking of hydrocarbon chains of UHMWPE with the formation of –OH and C–O bonds and the boundary layer of the filler and matrix, respectively, as well as a noticeable decrease in the peak intensity of the absorption band at 1462 cm^{-1} with an increase in the volumetric content of α-SiO_2 to 5% by volume.

2. On the IR spectra of all studied samples irradiated with a dose of 100 kGy, another additional peak of low intensity appears at 1717 cm^{-1}, which indicates the formation of bonds in ketones.

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ИК-СПЕКТРЫ γ-ОБЛУЧЕННЫХ НАНОКОМПОЗИТОВ СВЕРХВЫСОКОМОЛЕКУЛЯРНОГО ПОЛИЭТИЛЕНА / α-SiO_2

Р.С. Исмайилова, М.М. Кулиев, Г.А. Ахундова

С использованием FTIR-технологии исследовано влияние концентрации нанодобавки α-SiO_2 и гамма-радиации на FTIR-спектры чистых полимерных (сверхвысокомолекулярный полиэтилен (СВМПЭ)) и наполненных до разной (0, 1, 3, 5 об.%) концентрации α-SiO_2 пленок. Образцы облучали до доз: 0, 50 и 100 кГр источником ^{60}Co мощностью $3{,}3\cdot10^{-3}$ кГр/ч при комнатной температуре. Приведено соотношение полос поглощения с наличием соответствующих групп, а также показано наличие ряда характеристических полос поглощения композитов.

ІЧ-СПЕКТРИ γ-ОПРОМІНЕНИХ НАНОКОМПОЗИТІВ НАДВИСОКОМОЛЕКУЛЯРНОГО ПОЛІЕТИЛЕНУ / α-SiO_2

Р.С. Ісмайілова, М.М. Кулієв, Г.А. Ахундова

З використанням FTIR-технології досліджено вплив концентрації нанодобавки α-SiO_2 і гамма-радіації на FTIR-спектри чистих полімерних (надвисокомолеклярний поліетилен (НВМПЕ)) і наповнених до різної (0, 1, 3, 5 об.%) концентрації α-SiO_2 плівок. Зразки опромінювали до доз: 0, 50 і 100 кГр джерелом ^{60}Co потужністю $3.3\cdot10^{-3}$ кГр/год при кімнатній температурі. Наведено співвідношення смуг поглинання знаявністю відповідних груп. Показано наявність ряду характеристичних смуг поглинання композитів.