

RADIATION DAMAGES OF ISOTACTIC POLYPROPYLENE NANOCOMPOSITES WITH MULTI-WALLED CARBON NANOTUBES

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The crystal structure, IR absorption spectra and photoluminescence of isotactic polypropylene composites with multi-walled carbon nanotubes with concentrations ranging from 0.1 to 5.0 wt.% are investigated. The effect of radiation damages on structuring properties of composites under electron irradiation ($E_e = 1,8$ MeV) with absorption doses 3.0 and 4.0 MGy were considered. It is shown that sensitization of polypropylene by nanotubes promotes the crystallization of composites and leads to changes in the intermolecular interactions. Irradiation is difficult influences on the structure and processes of composites degradation are dependent on the content of nanotubes and irradiation dose.

INTRODUCTION

Polymer nanocomposites with unique fillers, including carbon nanotubes acquire exceptional optical, electronic, magnetic, mechanical and thermal properties [1]. Since carbon nanotubes have high polarization, it provides additional opportunities to improve composites due to rotational alignment of nanoparticles in electric fields [2].

Important role in the composite polymer material modification plays an adhesion degree at the interface of components, which is determined by the interaction of molecular components of macromolecules with carbon nanoparticles [3]. Since the aromatic groups, which are present in different families of vinyl monomers, are effective traps of radicals, it allows to implement their interaction with carbon nanotubes. Such interaction by covalent bonding forces results in attachment of polymer chains by nanotubes, and radical migration over traps [4]. Presence of above mentioned interaction even at small amounts of reinforcing particles (nanotubes) contributes to significant improvement of many operational properties of polymers. Thus, in single-walled carbon nanotube composites (SWCNT) with polypropylene (PP) produced by extrusion in the form of fibers that contain only 1.0 wt.% SWCNT an increase in tensile strength by 40% compared with pure PP and elastic modulus increased by 55% was observed [5]. Increase of SWCNT concentrations to 5 wt. % leads to a rise in strength by 90%, elastic modulus by 150% and conductivity by 340% [6]. Likewise, creating composites of multi-walled carbon nanotubes (MWCNT) also increased tensile strength and modulus of elasticity [7]. Presence of intermolecular interactions with nanotubes is evident from the transformation of the vibrational spectra of nanoparticles, in particular, a remarkable shift of Raman scattering band D*, associated with breathing vibrational mode, which occurs due to disordering of carbon nanotubes structure

[1, 3, 8, 9]. Obviously, the nature of interaction of polymer molecules with carbon nanotubes and effectiveness of composites properties modification depend on the components and conditions of preparation. In particular, it is important the possibility of supramolecular structures formation in polymer matrix, since carbon nanotubes are centers of crystallization. Naturally, the ratio of crystalline and amorphous phases, especially in the case of polymer macromolecules that interact with rigid nanotubes, affects the strength properties of nanocomposites.

On the other hand, the presence of nanoparticles characterized by strong acceptor properties within donor matrix should significantly act on the vibrational and electronic properties of both polymers and nanotubes by creating photogenerating complexes with charge-transfer. Noticeable modification of these properties can be achieved by ionizing radiation, which causes the proceeding of various radiation-chemical processes, in particular the appearance of ionized excited molecules, free radicals with subsequent formation and disappearance of double bonds. It is known that these processes during irradiation lead to cross-linking or degradation of molecular chains, which may create additional chemical effect and determine the changes in the physical properties of polymers.

In this paper we investigate the impact of high-energy electron irradiation on the crystalline and vibrational structure and photoluminescence of polypropylene composites with multiwalled carbon nanotubes.

1. EXPERIMENTAL

Multi-walled carbon nanotubes were synthesized by the combustion of a gaseous mixture of ethylene and hydrogen in the presence of iron-containing mixed metal hydroxides as catalysts dispersed.

Later nanotubes purified from mineral impurities by etching in solution $\text{NH}_4\text{F}:\text{HF}:\text{H}_2\text{O}:\text{HCL}$ with the specific ratio of components.

The composites of isotactic polypropylene (i-PP) with multi-walled nanotubes (MWCNT) was obtained in the form of fibers, which also produced the film composites. The concentration of nanotubes was equal to 0.1, 0.5, 1.0, 3.0 and 5.0 wt.%. The investigation of the crystal structure of the composites was carried out by X-ray diffraction. The vibrational spectra was carried out in the infrared region in the frequency range $450\text{--}4000\text{ cm}^{-1}$ using FTIP – spectrometer with a spectral resolution of 4 cm^{-1} . Photoluminescence spectra were investigated using an argon laser with a wavelength of $= 514,5\text{ nm}$ and using the monochromator MDR-3. The photoemission measurements were carried out at the temperature (77K). Laser power was 0.5 W/cm^2 .

Electron irradiation was carried out by using a linear electron accelerator ILU-6. The energy of bombarding particles was $E_e = 1,8\text{ MeV}$, absorption doses equal to 3.0 and 4.0 MGy. The temperature during irradiation did not exceed $\sim 333\text{ K}$.

2. RESULTS AND DISCUSSION

Macromolecules of isotactic polypropylene (i-PP), the conformation of which generally corresponds to helix 3_1 has a structural organization that can be described by monoclinic unit cell. Parameters of the cell are the following values: $a = 0,66$; $b = 2,096$; $c = 0,65\text{ nm}$, $\alpha = 90^\circ$; $\beta = 99,3^\circ$; $\gamma = 90^\circ$.

The X-ray diffraction pattern of nanocomposite i-PP/MWCNT is shown in Fig. 1. In the case of filling i-PP with multi-walled carbon nanotubes with different concentration, α -modification of crystalline structure is maintained. However, with the increasing content of nanotubes changes in relative intensities of individual interference maxima were observed. Especially notable is the relative decrease in the intensity of reflex (040) compared with the intensity of the line (110).

There is increased intensity peak (111) compared with reflex (131). It is obvious that in the crystalline regions of the reorientation of the crystallites, which causes a change in texture. This change is noticeable in the case of 0.1 wt.% MWCNT content at which the intensity of reflex (040) becomes less than the intensity of the line (110). Restructuring of texture is due to the fact that in the case of small content nanotubes are the nucleation centers of crystal phase and due to interaction with macromolecules of i-PP form a specific orientation of crystallites.

Despite the fact that with increasing concentration of nanotubes X-ray scattering intensity decreases, the diffraction peaks of MWCNT did not appear.

Irradiation of i-PP and its composites with high energy electrons with absorption doses of 3.0 and 4.0 MGy does not affect the monoclinic structure, but leads to changes in the intensities of individual lines, their displacement, the ratio between the amorphous and crystalline component, Fig. 2–3.

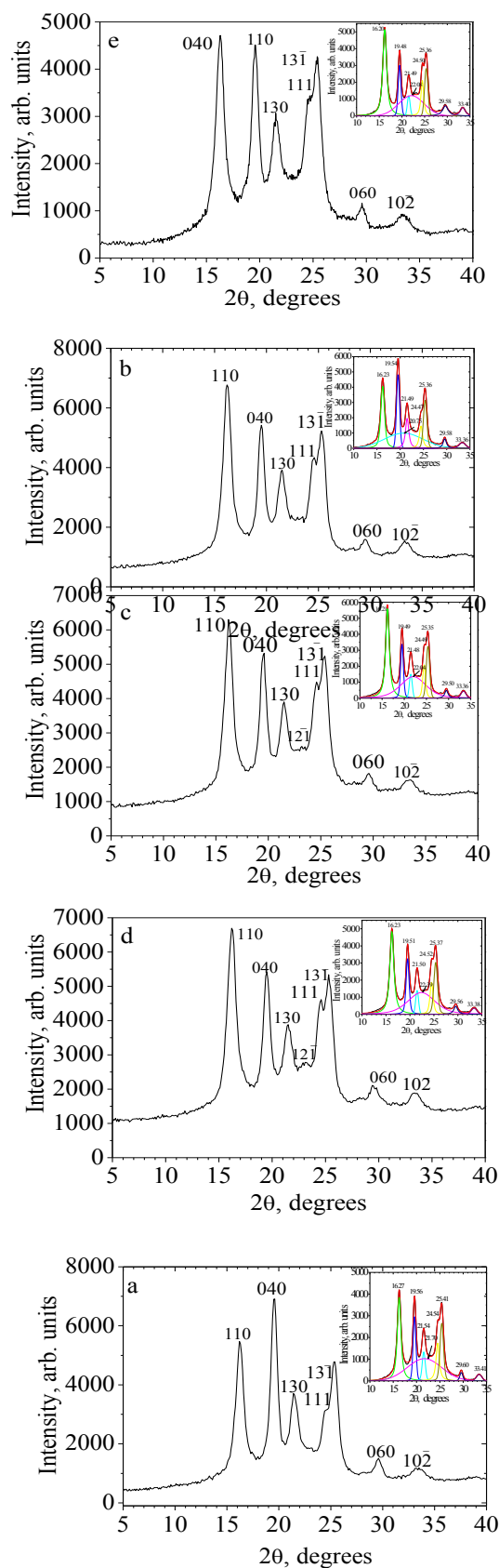


Fig. 1. Diffraction patterns of i-PP nanocomposites with 0.1 (a), 0.5 (b), 1.0 (c), 3.0 (d) and 5.0 wt.% MWCNT (e) (the inserts: decomposition for the amorphous and crystalline components and the diffraction angles 2θ)

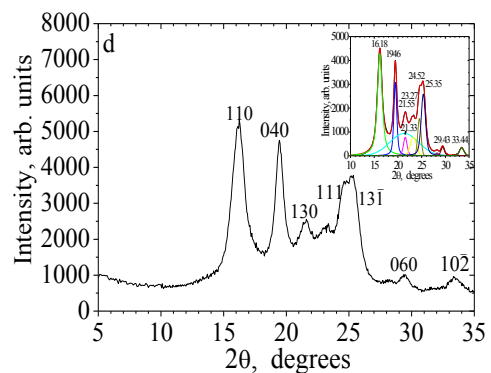
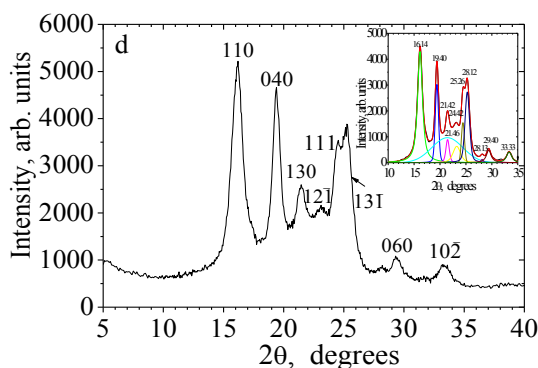
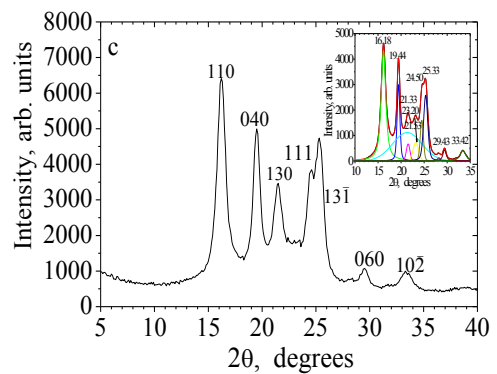
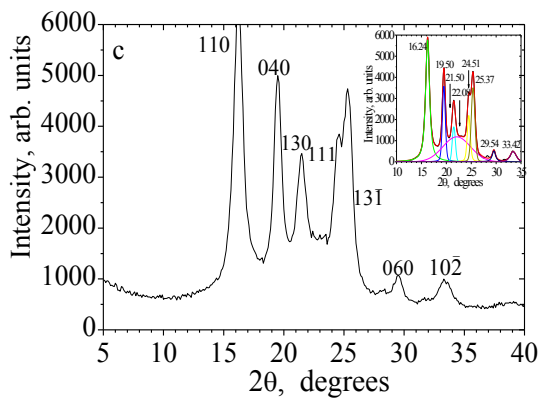
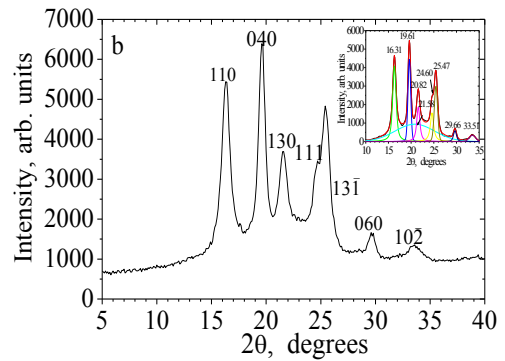
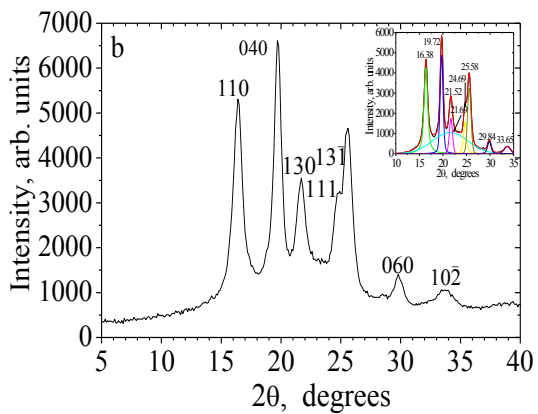
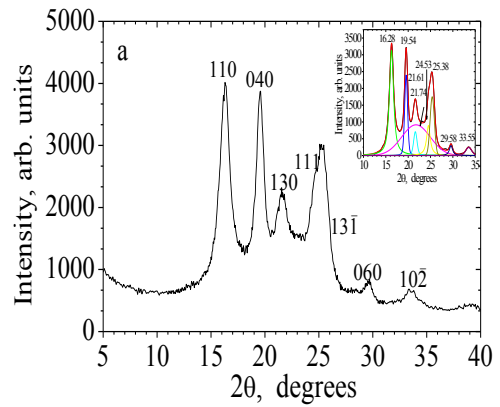
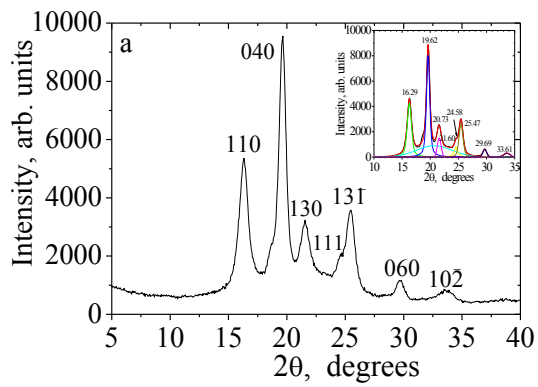


Fig. 2. Diffraction patterns of *i*-PP(a) and nanocomposites with 0.5 (b), 1.0 (c), 3.0 wt.% (d) MWCNT after electron irradiation with absorption dose 3.0 MGy (the inserts: decomposition for the amorphous and crystalline components and the diffraction angles 2θ)

Fig. 3. Diffraction patterns of *i*-PP (a) and nanocomposites with 0.5 (b), 1.0 (c), 3.0 wt.% (d) MWCNT after electron irradiation with absorption dose 4.0 MGy (the inserts: decomposition for the amorphous and crystalline components and the diffraction angles 2θ)

Intra-and intermolecular structure of i-PP and its nanocomposites with different content of MWCNT after high-energy electron irradiation was studied using infrared absorption. On Fig. 4 it is shown the transmission spectrum in the infrared range of the i-PP, from which it is seen the presence of many inherent lines of crystalline and amorphous phases and different conformations of 3_1 helical chain.

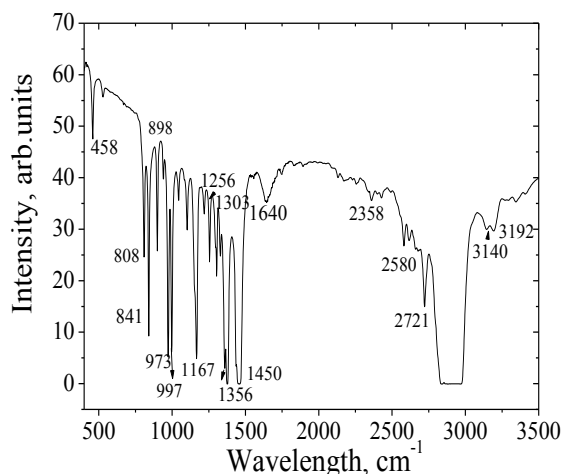


Fig. 4. IR transmission spectrum of i-PP

In the transmission spectra it is seen a set of lines with frequencies 458, 808, 841, 898, 973, 998, 1167, 1256, 1303, 1375, 1450, 1640, 2358, 2580, 2721, 2868...2956, 3140, 3192 cm⁻¹.

Intensive absorption band at 1450 cm⁻¹ is not related to atacticity of PP. Presence of absorption bands at 841, 973, 997, 1167 cm⁻¹ points out the isotactic conformation of PP. Moreover, lines at 867 and 962 cm⁻¹ inherent to syndiotactic PP are missing in spectra. Bands at 808, 841, 898, 997 and 1167 cm⁻¹ refer to crystalline phase. The main conformation of i-PP macromolecules corresponds to 3_1 spiral with three monomeric units. Spiral conformation within crystal phase possesses line at 808 cm⁻¹ resulting from splitting of a band at 830 cm⁻¹ characteristic for amorphous phase during crystallization of i-PP. This line exists in all modifications. Nearby position 841 cm⁻¹ is the line that corresponds to the formation of long monomer units in crystalline phase ($n > 10$) in the mixed alternating sequence of trans-gauche spiral conformation 3_1 . Band at 997 cm⁻¹ occurs due to building crystal lattice from spiral segments with $n > 10$.

Band at 973 cm⁻¹ characterize presence of trans-gosh conformers with $n > 4$ in amorphous phase. Near 1167 cm⁻¹ line there is a shoulder at 1151 cm⁻¹, corresponding to folded into a tangle conformation that is present in liquid state and amorphous region.

In the infrared absorption spectrum it is also observed several possible lines that are associated with the presence of skeletal stretching C-C. These are lines 973, 1358 and 1378 cm⁻¹, already mentioned bands at 1151 and 1167 cm⁻¹. The bands at 808, 940, 1103 cm⁻¹ correspond to stretching vibrations of C-CH₃.

Availability of α , β , γ , and smectic crystal structure modifications in addition to restructuring of IR-absorption spectra within the region of helical conformations between 808 and 841 cm⁻¹ leads to changes in the stretching vibration of CH₂ and CH₃ groups. Bands corresponding to stretching vibrations of C=C bonds near 1556 and 1640 cm⁻¹ and =CH bonds at 3140 and 3192 cm⁻¹ are also important for consideration.

Spectra of IR transmission for i-PP with 0.5 wt.% of MWCNT is shown on Fig. 5. Likewise for i-PP in IR-absorption spectra of nanocomposite with 0.5 wt.% of MWCNT, lines corresponding to crystal (808, 841, 898, 997, 1167 cm⁻¹) and amorphous phases (973, 1151 cm⁻¹) are observed.

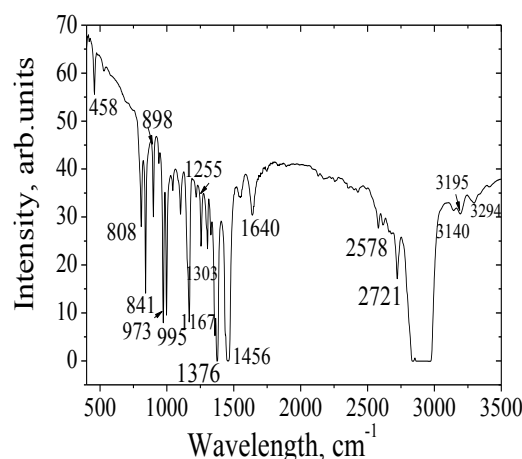


Fig. 5. IR transmission spectrum of nanocomposite i-PP with 0.5 wt.% MWCNT

At the same time, it is seen the decrease of absorption of low-frequency region below 800 cm⁻¹ and of bands related to crystal (808, 841, 898, 995, 1167 cm⁻¹) and amorphous (973 cm⁻¹) phases and to C-C bonds (1358 cm⁻¹).

Moreover, band associated with spiral conformation of macromolecules in crystal phase, shifted to 995 cm⁻¹. While intensity of lines at 808 and 898 cm⁻¹ lowered not substantially, its decrease in case of line positioned at 841 cm⁻¹, which corresponds to the presence of trans-gosh sequences in spiral conformation of macromolecules of crystal phase, is more obvious. Although, it is seen the increase of absorption lines at 1551 and 1640 cm⁻¹, which associated with unsaturated bonds C=C.

In Fig. 6 it is shown the IR-transmission spectra of i-PP with 1.0 wt.% of MWCNT. It is seen that throughout the whole frequency range the background absorption increases sharply compared to nanocomposite i-PP with 0.5 wt.% MWCNT. At the same time, absorption changes in the region of specific lines. Thus, the absorption of bands at 808 and 898 cm⁻¹ slightly increased while decreased near for 841 and 995 cm⁻¹. In addition, there was a slight drop in the absorption near 973 cm⁻¹.

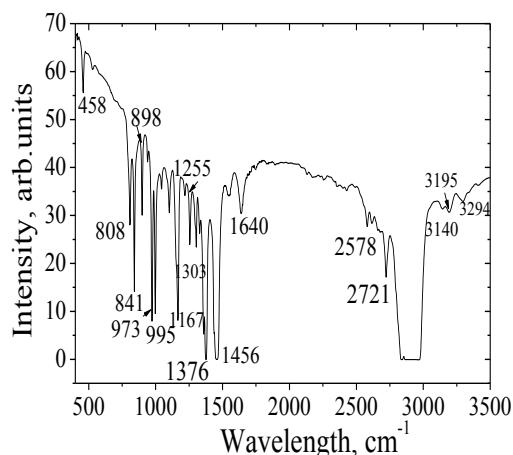


Fig. 6. IR transmission spectrum of nanocomposite *i*-PP with 1.0 wt.% MWCNT

In the case of *i*-PP with 3.0 and 5.0 wt.% of MWCNT a sharp increase in infrared absorption was observed, Fig. 7.

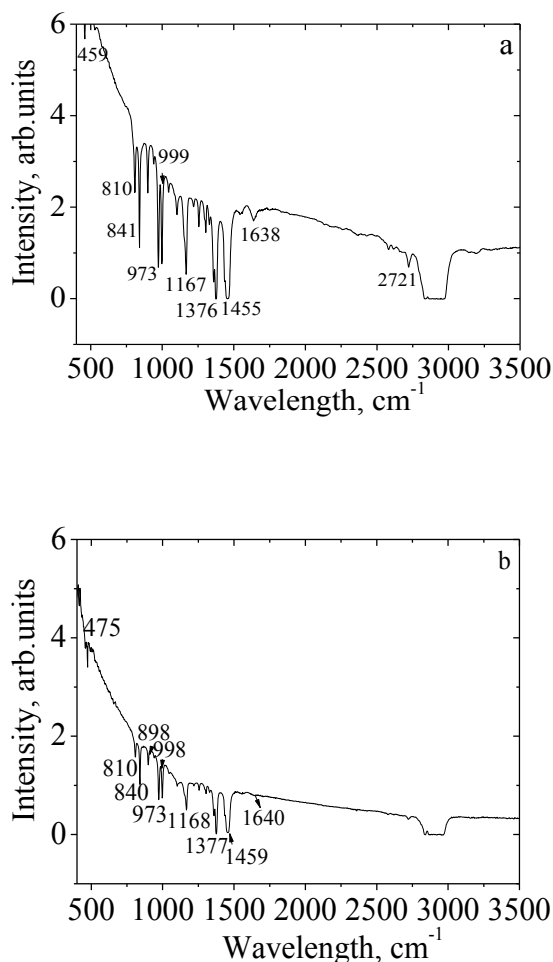


Fig. 7. IR transmission spectra of nanocomposites *i*-PP with 3.0 (a) and 5.0 wt.% MWCNT (b)

Transmission over the entire range of frequencies displays very small amplitude (0...6%). However, the absorption peaks of nanotubes that should reside near 873 and 1581 cm^{-1} are absent, but all the lines inherent in *i*-PP were kept. Frequencies as well as relative intensities of these lines remain almost unchanged, indicating a negligible effect of nanotubes at significant concentrations on the supramolecular organization and structure of *i*-PP. Obviously, the nanotubes tend to aggregate, which is more prominent at higher concentrations, thus, the effect of these fillers on intra- and intermolecular structure of *i*-PP structure turns out insignificant. As follows from the analysis of infrared absorption behavior for non-irradiated nanocomposites of *i*-PP filled with MWCNT, only at small concentrations of nanotubes (0.5 wt.%) it is observed a substantial reconstruction of the spectrum, related mainly to the change in relative intensities of transmission bands corresponding to crystal and amorphous phases, spiral conformation, C-C, C=C bonds and polyenic sequences.

Restructuring of the electronic structure of polymers and the presence of different types of impurities, and polyene sequences in polymers initiates the appearance of photoluminescence in polymers, and for different excitation wavelengths these spectra differ substantially.

Fig. 8 shows the photoluminescence spectra (PL) of *i*-PP obtained at different excitation wavelengths.

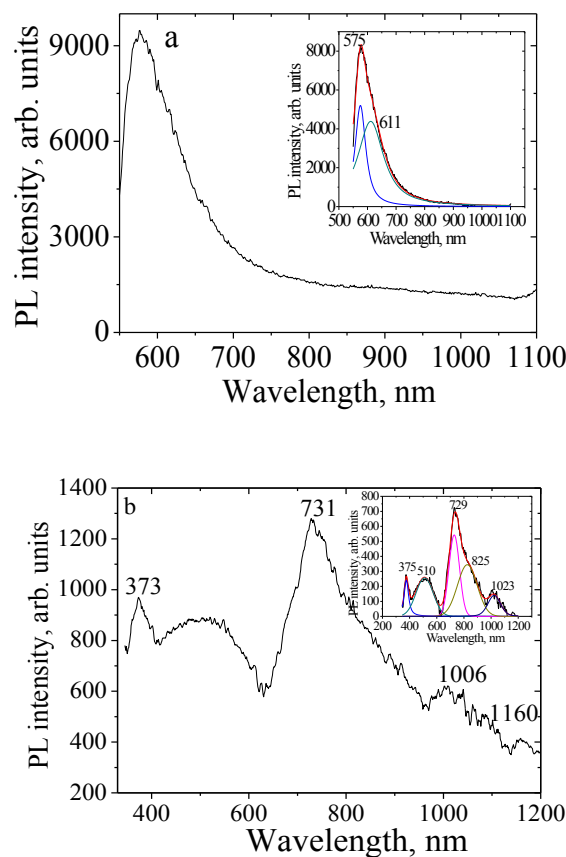


Fig. 8. The photoluminescence spectra of *i*-PP at excitation wavelengths of 514.5 (a), 337 nm (b) and the temperature of 77 K. (The insets: decomposition of PL spectra for components)

In case of $\lambda_{ex}=514.5$ nm strong emission band with a maximum at 600 nm is observed. This band is wide enough and asymmetric allowing to describe its by two components with maxima near 581 and 625 nm.

Excitation wavelength $\lambda_{ex}=337$ nm provides a complex spectrum in a wide range of 300...1200 nm. In this range the PL spectrum decomposition into components can be performed by peaks at 375, 510, 729, 825 and 1023 nm.

Photoirradiation of isotactic PE does not cause any fluorescence spectrum as in *i*-PP there is no polyene structures with long sequences. It can be assumed that the carbonyl groups C=O do not participate in the creation of the PL spectra in the *i*-PP. The emergence of intensive PL band in the polymer is due to the transition $\pi \rightarrow \pi^*$, which corresponds to the unsaturated bonds C=C and maybe dienes. Absorption implemented in these structures leads to the appearance of two components of the emission at 581 and 625 nm in the PL spectra. It is possible that the asymmetry of the PL band in the long-wave region indicates the existence of *i*-PP polyene structures with longer sequences, but their number is very small and thus revealing their presence when the excitation wavelength $\lambda_{ex}=514.5$ nm is impossible. However, the appearance of the PL spectra at $\lambda_{ex}=337$ nm indicates the presence of conjugated structures with of sequences significant lengths. From comparison of the PL intensities obtained at different λ_{ex} , it is obvious that the number of long sequences is insignificant.

The band at 375 nm, as well as for PE, probably corresponds to a set of narrow lines that appear in the PL spectra as a result of broken C-C bonds recombination. All other PL bands are caused by conjugated structures with sequences of different lengths of. If a broad band with a peak at 510 nm is associated with a set of unsaturated structures with short sequences, the other bands correspond to longer chains. A sufficiently intense band with a maximum at 729 nm is distinguished. We can assume the high content of polyene sequences of distinct lengths, leading to the appearance of this emission bands. It is seen that in *i*-PP there are also conjugated structures with rather long sequences that lead to irradiation concentrated in a broad band with a maximum at 1023 nm. Ionizing electron irradiation and filling polymer with carbon nanotubes affects the formation of unsaturated and polyene structures in *i*-PP insignificantly, even with large absorption doses. For absorption dose of 3.0 MGy PL spectra change little for *i*-PP and its nanocomposites with 0.5 and 1.0 wt.% of MWCNT, Fig. 9.

Similarly, a small rearrangement of the conjugated structure occurs for *i*-PP and its nanocomposites with 0.5 wt.% of nanotubes after electron irradiation with absorption dose of 4.0 MGy, Fig. 10.

It is seen that only for the nanocomposite with 1.0 wt.% of nanotubes there is the emergence of polyene structures with longer sequences.

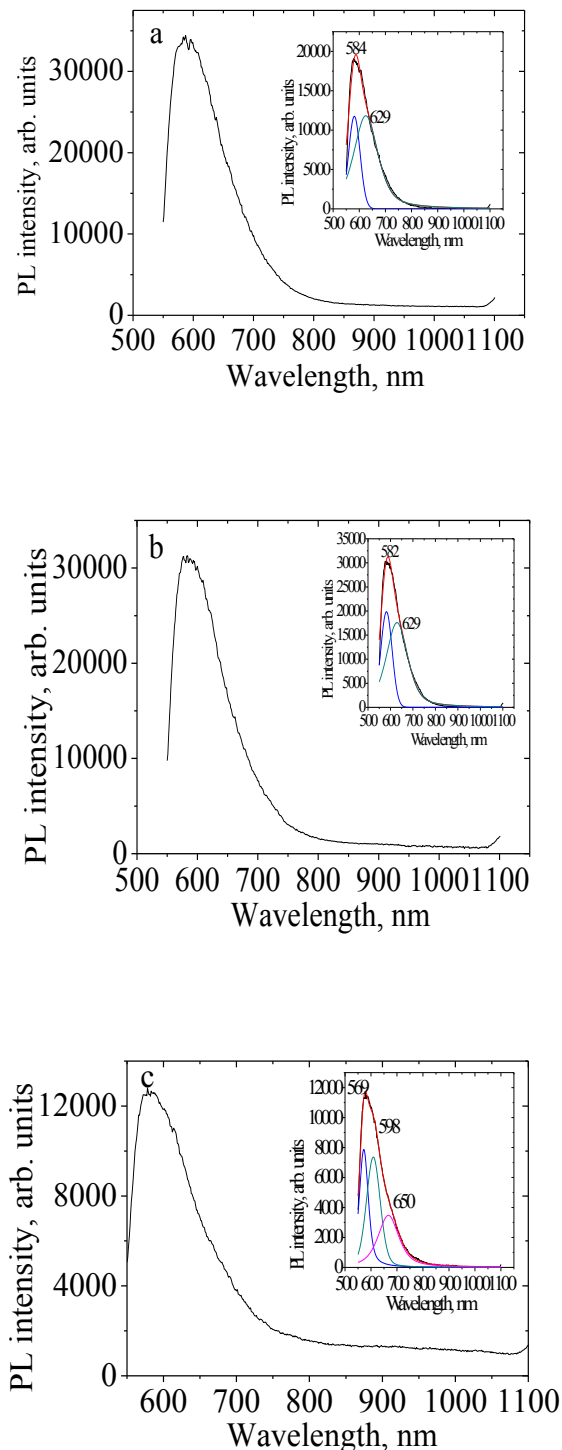


Fig. 9. The photoluminescence spectra of *i*-PP (a) and nanocomposites with 0.5 (b) and 1.0 wt.% MWCNT (c) after electron irradiation with absorption dose 3.0 MGy ($\lambda_{ex}=514.5$ nm)

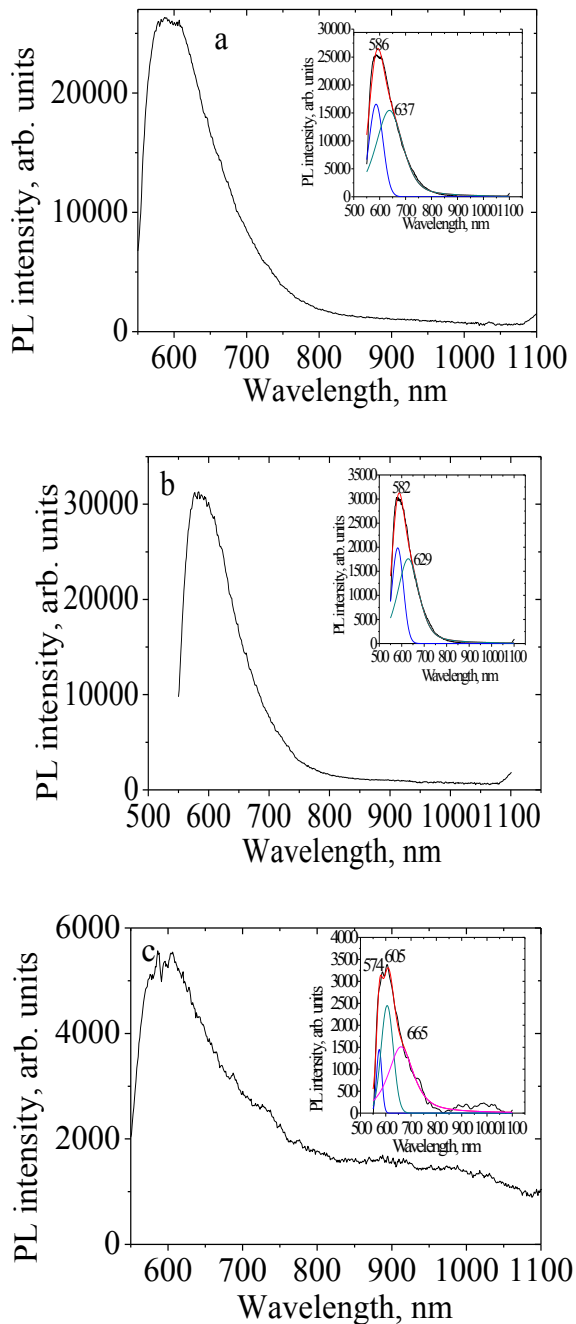


Fig. 10. The photoluminescence spectra of i-PP (a) and nanocomposites with 0.5 (b) and 1.0 wt.% MWCNT (c) after electron irradiation with absorption dose 4.0 MGy ($\lambda_{ex} = 514.5$ nm)

CONCLUSIONS

Reinforcement of isotactic polypropylene with multiwalled carbon nanotubes affects the crystal, vibrational and electronic structure of composites. With increasing content of nanotubes within 0.1...5 wt.% sensitizing role of nanoparticles increases, which is a sign of the changing nature of the interaction at the interface between the polymer matrix and nanotubes.

Radiation damage in electron irradiation leads to the simultaneous processes of degradation of macromolecules and their crosslinking.

In the initial state in isotactic polypropylene conjugated sequences available that form the PL spectra, both at low $\lambda_{ex} = 337$ nm and longer excitation wave $\lambda_{ex} = 514.5$ nm wavelengths. In i-PP nanocomposites with MWCNT at concentrations up to 1.0 wt.% PL spectra have the form similar to the form for i-PP and nanotubes have little effect on the formation of polyene sequences. With the growth of nanotubes content up to 5.0 wt.% PL spectra change significantly, indicating the formation of i-PP polyene sequences of different lengths.

At high absorption doses, 3.0 and 4.0 MGy and MWCNT concentrations to 1.0 wt.% nanotubes have little effect on the formation of polyene sequences and radiation crosslinking of macromolecules.

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РАДИАЦИОННЫЕ ПОВРЕЖДЕНИЯ НАНОКОМПОЗИТОВ ИЗОТАКТИЧЕСКОГО ПОЛИПРОПИЛЕНА С МНОГОСТЕННЫМИ УГЛЕРОДНЫМИ НАНОТРУБКАМИ

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Исследована кристаллическая структура, ИК-спектры поглощения и фотолюминесценции композитов изотактического полипропилена с многостенными углеродными нанотрубками с концентрациями от 0,1 до 5,0 вес.%. Влияние радиационных повреждений на структурирование композитов рассмотрено при электронном облучении ($E_e = 1,8$ МэВ) с дозами поглощения 3,0 и 4,0 МГр. Показано, что сенсбилизация полипропилена нанотрубками способствует кристаллизации композитов и приводит к изменению межмолекулярного взаимодействия. Облучение сложным образом влияет на процессы структурирования и деградации композитов, которые зависят от содержания нанотрубок и дозы облучения.

РАДІАЦІЙНІ ПОШКОДЖЕННЯ НАНОКОМПОЗИТІВ ІЗОТАКТИЧНОГО ПОЛІПРОПІЛЕНУ З БАГАТОСТІННИМИ ВУГЛЕЦЕВИМИ НАНОТРУБКАМИ

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Досліджено кристалічну структуру, спектри ІЧ-поглинання та фотолюмінесценції композитів ізотактичного поліпропілену з багатостінними вуглецевими нанотрубками з концентраціями від 0,1 до 5,0 ваг.%. Вплив радіаційних пошкоджень на структування композитів розглянуто при електронному опроміненні ($E_e = 1,8$ МеВ) з дозами поглинання 3,0 і 4,0 МГр. Показано, що сенсбілізація поліпропілену нанотрубками сприяє кристалізації композитів і призводить до зміни міжмолекулярної взаємодії. Опромінення складним чином впливає на процеси структування і деградації композитів, які залежать від вмісту нанотрубок і дози опромінення.