

Radiation damage of isotactic polypropylene composites with multi-walled carbon nanotubes

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The crystal structure, IR absorption, and photoluminescence spectra of isotactic polypropylene composites with multi-walled carbon nanotubes (MWCNT) have been studied. MWCNT concentrations in the range from 0.1 to 5 wt. % are investigated. The influence on the structure and the destruction of the composites during electron irradiation ($E_e = 1.8$ MeV) at the absorption doses between 3.0 and 4.0 MGy has been examined. It has been shown that the sensitization with the MWCNT contributes to the crystallization of the composites and causes changes in the molecular interaction. The irradiation influences in a complex manner the composite structuring and degradation processes that depend on the MWCNT content and radiation dose.

Исследованы кристаллическая структура, спектры инфракрасного поглощения и фотолюминесценции композитов изотактического полипропилена с многостенными углеродными нанотрубками с концентрацией от 0,1 до 5 масс.%. Влияние радиационных повреждений на структурирование композитов рассмотрено при электронном облучении ($E_e = 1,8$ МэВ) с дозами поглощения 3,0 и 4,0 МГр. Обнаружено, 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.

Nanocomposites of polymeric matrices with nanoparticles of unique ordered structure (in particular, fullerenes and carbon nanotubes) exhibit extraordinary optical, electronic, magnetic, mechanical, and thermal properties [1]. Since fullerenes and carbon nanotubes (CNT) have a high polarizability, they offer additional possibili-

ties of improvement in the properties of composite films or fibers. This is due to the oriented arrangement of nanoparticles in electric fields [2].

In the modification of composite polymeric materials, of a great importance is the adhesion degree of the components at the interface. This is defined by the interac-

tion of molecular components of macromolecules with carbon nanoparticles [3]. Since aromatic groups are effective traps of free radicals, the presence of the radical initiators in different families of vinyl monomers makes possible their capturing with CNT. This results in a fastening of the polymer chains by CNT due to their interaction. It is caused by covalent binding forces as well as by the migration of radicals on the traps [4]. The presence of such interaction even at a small amount of reinforcing particles contributes to a substantial improvement in various performance properties of polymers. For example, composites of single-walled CNT (SWCNT) with polypropylene (PP) were prepared by extrusion in the form of fibers containing only 1 wt. % of SWCNT have shown 40 % increase in the tensile strength in comparison with pure PP and the moduli grew by 55 % [5]. The increase in the SWCNT concentration up to 5 wt.% resulted in the strength increase by 90 %, moduli by 150 %, and conductivity by 340 % [6]. Similarly, the composites with multi-walled CNT (MWCNT) show also increased tensile strength and elasticity modulus [7].

The presence of molecular interaction with the CNT was confirmed by changes in vibrational spectra of the nanoparticles. A noticeable shift of the Raman scattering band is connected with the breathing vibrational mode, which appears through the disordering of the CNT structure [1, 3, 8–9]. It is obvious that the nature of the interaction between the flexible chain molecules of the polymers with the CNT and the effectiveness of the performance modification depend on the composite components and the preparation conditions. In particular, of importance is the formation possibility of supramolecular structures in the polymeric matrix, since the CNT are the crystalline phase nucleation centers. It is natural that the content ratio of crystalline and amorphous components, especially in the case of flexible-chain macromolecules of polymers interacting with the rigid CNT, will influence the strength properties of the nanocomposites.

On another hand, the presence of nanoparticles with strong acceptor properties in a donor matrix must influence substantially the vibrational and electronic properties both of polymers and nanotubes. This is caused by the appearance of photo-generated charge-transfer complexes. An appreciable modification of these properties

being reflected in the nature of the appearing molecular interactions could be achieved under an ionizing radiation. This causes different radiation-chemical processes, in particular, formation of ionized excited molecules and free radicals. The subsequent formation and disappearance of double bonds, exchange, migration, recombination, and free valences could follow. These processes under irradiation are known to result in the cross-linking of molecular chains or destruction thereof. That could cause an additional chemical effect and define changes in physical properties of the polymers. In this work, the influence of electron irradiation on the crystalline and vibrational structures and the photoluminescence of isotactic polypropylene composites with the MWCNT has been studied in detail.

The MWCNT used in this study were obtained as cathode deposits in the DC arc vaporization process of graphite. The arc discharge conditions and the apparatus used are described in details elsewhere [10]. The anode was a graphite rod (6.2 mm diameter, 10 mm length) with a hole (5.1 mm diameter, deeper than the burned part of the electrode) filled with a mixture of Ni (4.2 %) and Y (2 %) oxides and graphite powder. The cathode was a graphite rod (15 mm diameter, 15 mm length). The purity of the graphite rods and powder was 99.999 % (ash residue <500 ppm). The gap between the graphite electrodes (0.5–1.5 mm) was kept by manually advancing the consumed anode. The discharge voltage and current varied between 20–25 V and 37–45 A, respectively. The discharge time was between 50 and 120 s at N₂ pressure of 700 mbar.

As reported before, MWCNT can be found in the inner black core of the cathode deposit (Fig. 1). This figure shows the SEM images of the sample inside the (2Y:4.2Ni) cathode deposit at several magnifications. The MWCNT are straight and have various diameters up to more than 100 nm. Besides the MWNTs, other carbon species can be seen. The MWCNT are embedded in a mixture of graphitic nanoparticles. The content of MWCNT inside the (2Y:4.2Ni) cathode deposit is estimated to be in the range of 60 to 70 %. The carbon impurities were oxidized in air at 425°C and the remaining material where hold for 3 hours in concentrated HCl. This procedure was repeated until the Ni content in the material below 1 %. The products were analyzed by scanning electron microscopy (SEM), high-resolution transmission electron microscopy

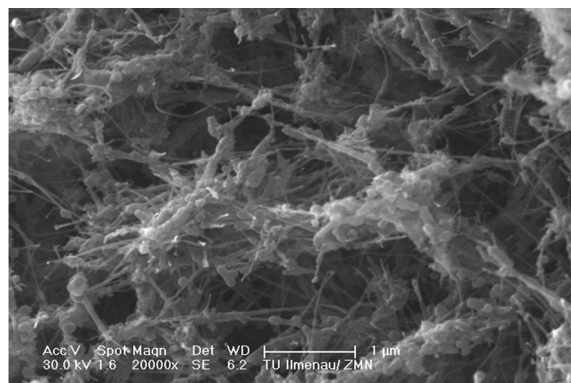


Fig. 1. SEM microphoto of the inner core of the cathode deposit. The image reveals the presence of MWCNTs inside the cathode deposit.

(HR-TEM) and thermogravimetric analysis (TG). From SEM and TG data, the content of MWCNT in the samples was estimated to exceed 90 %.

The composites of isotactic polypropylene (iPP) with MWCNT were obtained in the form of fibers. The composite films were made from these fibers, too. The CNT concentration was equal to 0.1, 0.5, 1.0, 3.0 and 5.0 wt.%. The crystal structure of the fibers was examined by X-ray diffraction. The vibrational spectra were studied in the IR region of 450–4000 cm^{-1} using a FTIR spectrometer with the spectral resolution of 4 cm^{-1} . The photoluminescence spectra were investigated under excitation of the samples by the emission of an argon laser harmonic ($\lambda = 514.5 \text{ nm}$) using an MDR-3 monochromator. The photoemission was measured at temperatures of liquid helium (4.2 K) and nitrogen (77 K). The laser power was attenuated by filters down to values less than 0.5 W/cm^2 . This power attenuation was selected to decrease the photo-induced changes and to avoid an initial heating of the samples. Irradiation with electrons was carried out using a linear electron accelerator. Energy of bombarding particles was $E_e = 1.8 \text{ MeV}$, the absorption doses 3.0 and 4.0 MGy. The temperature during the irradiation experiments did not exceed 320 K.

The macromolecules of iPP with conformation mainly corresponding to the 3_1 helix with three monomer units per one turn have a structural organization that can be described as a monoclinic unit cell with the following parameters: $a = 0.66$; $b = 2.096$; $c = 0.65 \text{ nm}$, $\alpha = 90^\circ$; $\beta = 99.3^\circ$; $\gamma = 90^\circ$. The cell contains 12 monoclinic units. Fig. 2 shows the X-ray diffraction picture from the films of iPP/MWCNT nanocomposites. An increase of CNT content in the samples

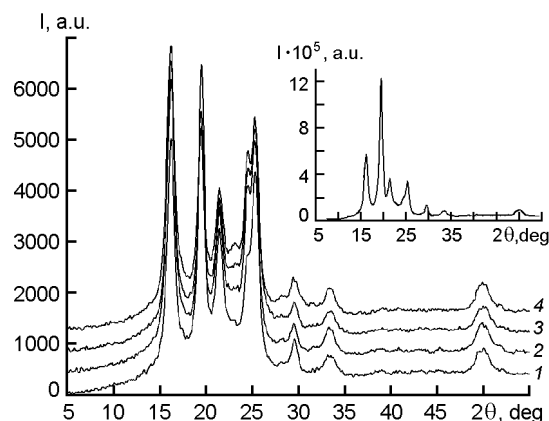


Fig. 2. X-ray diffraction patterns from the iPP/MWCNT film nanocomposites with various content of CNT (wt. %): 0.5 (1); 1.0 (2); 3.0 (3); 5.0 (4). Inset: similar pattern for the undoped iPP ($\lambda_{C0} = 0.179 \text{ nm}$).

increases the intensity of the X-ray peaks. The decomposition of the X-ray diffraction spectrum into components caused by the crystalline and amorphous phases indicates an increase in the topologically regulated phases with increasing CNT concentrations.

So, at 0.5 wt.% of MWCNT, 73.6 % of the composite is found in the crystalline state. In case of 1 wt.% MWCNT, the quantity of that phase is 73.9 %, at 3 wt.% of MWCNT — 74.6 % and at 5 wt.%, the increase is more essential (78.2 %). Thus, even at an essential content of crystalline components in the pure polypropylene, the presence of CNT contributes to its increase. On the other hand, as the concentration of CNT increases, the positions, the amplitude intensity values and the half-width of the diffraction reflections are changed. That indicates a change in the lattice parameters, texture, coherent scattering block sizes and micro-distortions. The effect of CNT on the supramolecular organization of polymeric macromolecules is a special feature of the lattice formation. In particular, as the concentration of CNT changes, an arrangement of those occurs [8], that affects the orientation of the crystals.

The interactions at the polymeric matrix/CNT interface influence the vibrational spectrum of the chromophore groups, even if the content of CNT is insignificant. This could be seen from the behavior in the IR absorption (Fig. 3).

The noticeable absorption bands at 840 and 998 cm^{-1} is characteristic for the bending vibrations in the crystalline phase [11]. At increasing CNT content, the intensity of these absorption bands grows, indicating

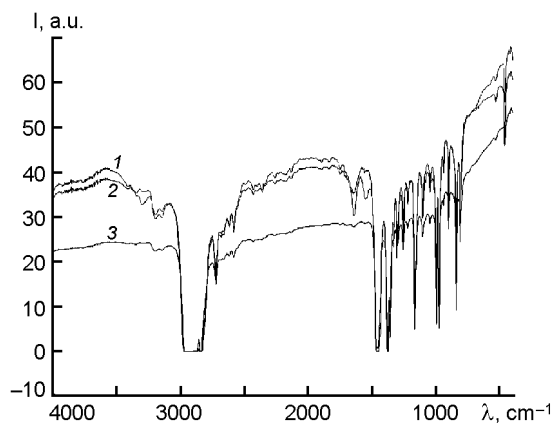


Fig. 3. IR absorption spectrum for the iPP/MWCNT film nanocomposites with various content of CNT (wt. %): undoped iPP (1); 0.5 (2); 1.0 (3).

the incorporation of helical segments into the crystal lattice and an increase in the number of chains consisting of the alternating trans-gauche-conformers. Furthermore, the intensity of the methyl groups pendulum swings near 600 cm^{-1} changes, as well as near 1550 and 1639 cm^{-1} . That also shows a change in the interaction nature between the molecular chains, which possibly is realized through their bonds with CNT. The presence of such an interaction influences the behavior of elementary electronic excitations. The increased photoluminescence in the emission band corresponding to about 2.1 eV (Fig. 4) is observed at low CNT content (0.1 and 0.5 wt.%) only.

A further increase in the CNT content results in the photoluminescence quenching, thus indicating the effective separation of the electron-hole pairs in the presence of the p-type impurities. This could be due to the formation of intermolecular donor-acceptor interaction, which defines the CNT influence on the supramolecular polymer structure. The above interaction contributes to the exchange, too. At increasing CNT concentration, the spectrum displacement towards the red region appears as well. Beginning from 3 wt.%, an emission maximum near 900 nm is formed. This could be due to a contribution from CNT to the electron spectrum reconstruction within the energy band gap.

The irradiation of polypropylene effects its structurization in a complex manner, since the polymer structure is an intermediate between the different polymer chains tending to intermolecular linking and degradation of the main molecular chain. The linking and degradation processes in

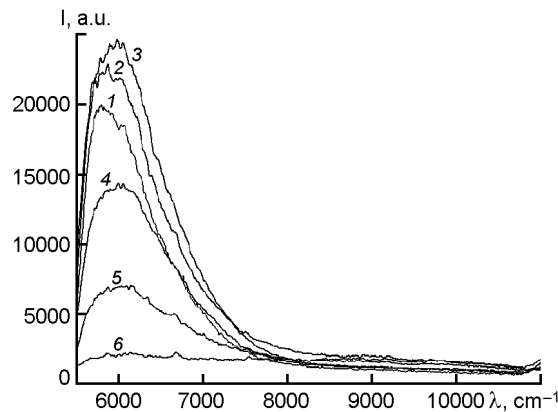


Fig. 4. Photoluminescence spectra of the iPP/MWCNT composite fibers with various content of CNT (wt. %): undoped iPP (1); 0.1 (2); 0.5 (3); 1.0 (4); 3.0 (5); 5.0 (6) ($\lambda_{ex} = 514.5\text{ nm}$, $T = 77\text{ K}$).

polypropylene occur approximately in an equal proportions. The occurrence and relation of these processes depend substantially on the bombarding particle type, energy and irradiation conditions. In such composites, the sensitizing components could influence predominantly either the structuring or degradation of polymers.

Fig. 5 shows the changes in the X-ray diffraction patterns for iPP and iPP/MWCNT composites at electron absorption doses 3.0 and 4.0 MGy , respectively. As the radiation dose increases, the intensity of the iPP diffraction peaks is seen to decrease. A sharp drop of the crystallinity with retention of the amorphous phase is observed. This made it possible to assume that the structurization of the polymer macromolecules deteriorates due to destruction thereof. The CNT introduction into the polymeric matrix slows down this process even at a low concentration of the nanoparticles. Beginning from 1 wt.% of MWCNT, the crystallization extent during the irradiation grows more substantially than for the unirradiated samples. At the absorption dose 3.0 MGy , some bands become broadened. In contrast, at the 4.0 MGy dose, this is not observed at all. It is obvious that the linking processes of the macromolecules are favored under irradiation of the composites as the radiation dose and CNT concentration are increased, thus improving the structurization of the samples. On the other hand, smaller doses of irradiation cause micro stresses, which could be relaxed at increasing exposure time.

The photoluminescence spectrum changes during the irradiation in a complex manner.

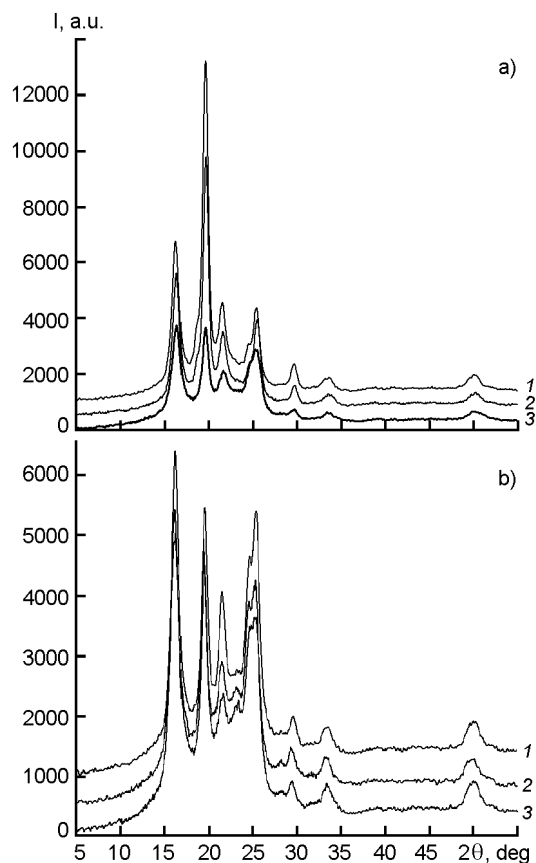


Fig. 5. X-ray diffraction undoped iPP (a) and its composites with 3.0wt% MWCNT (b) after irradiation with electrons ($\lambda = 0.179$ nm; $E_e = 1.8$ MeV). 1—no irradiation; 2—3.0; 3—4.0 MGy.

For the pure polypropylene, the emission band has different integrated intensity values depending on radiation dose, its position remaining unchanged during the irradiation. At increasing CNT concentration and radiation dose, the luminescence in the emission band decreases, except for the MWCNT content of 3 wt.% where it remains almost constant. So, the irradiation with electrons effects only slightly the radiation resistance of the composites.

Thus, the reinforcement of isotactic polypropylene with MWCNT influences the crystalline, vibrational and electronic structure of the composites. As the CNT content increases within limits of 0.1 to 5.0 wt.%, the sensitizing role of the nanoparticles increases, thus confirming a change in the interaction nature on the polymeric matrix/CNT interface. The radiation damages under electron irradiation result in the simultaneous macromolecule destruction and linking. In the pure iPP polymer, the processes of destruction are predominant, whereas in the composites, at the radiation dose increase to 3.0–4.0 MGy, the structuring plays more important role. Finally, that provides an increase in the polymer radiation resistance.

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Радіаційні пошкодження композитів ізотактичного поліпропілену з багатостінними вуглецевими нанотрубками

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Досліджено кристалічну структуру, спектри інфрачервоного поглинання і фотолюмінесценції композитів ізотактичного поліпропілену з багатостінними вуглецевими нанотрубками при концентраціях останніх від 0,1 до 5,0 мас. %. Вплив радіаційних пошкоджень на структурування композитів розглянуто при електронному опроміненні ($E_e = 1,8$ МеВ) з дозами поглинання 3,0 і 4,0 МГр. З'ясовано, що сенсibiлізація поліпропілену нанотрубками сприяє кристалізації композитів та призводить до зміни міжмолекулярної взаємодії. Опромінення складним чином впливає на процеси структурування і деградації композитів, які залежать від вмісту нанотрубок та дози опромінення.