UDC 541.16

ELECTRON AND VIBRATION STRUCTURE OF FLUORINE-CONTAINING POLYAMIDE FILM UNDER HIGH ENERGETIC ELECTRON IRRADIATION

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Influence of high energetic electron irradiation (E_i = 1.8 MeV) on the electron and vibrational properties of fluorine containing polyamide films was studied. Nature of electron transitions and vibration bands in Raman and IR-absorption spectra in the initial state of the film was determined by quantum-chemical calculations. Results of optical absorption, Raman scattering and IR-absorption showed that irradiation of the film with dose of 1 MGy does not lead to significant changes of electron and vibrational structure. Increase of the dose to 3 MGy influences the intensity of vibration bands in Raman and IR-absorption spectra. Films that were transparent in the initial state became yellow-colored and fragile after the irradiation.

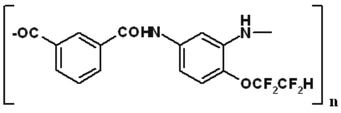
INTRODUCTION

Great part of studies in nowadays nanoscience and nanotechnology is dedicated to polymer-based composites filled with different nanostructures [1]. One of the directions in this field is polymers with carbon fillers that posses row of extraordinary physically-chemical properties and have practical applications in electronics, energy storage, sensing platforms, field emission devices, biological labeling ets. [2–3]. Among different polymers that are used as matrices for the fillers the most popular are polyamide ones that have charming thermoplastic with good process ability, chemical resistance [1, 4]. Irradiation with high-energetic charged particles (electrons, ions) of such nanocomposites often leads to improvement of mechanical properties and appearance of new useful characteristics [5]. The carbon fillers such as fullerenes, nanotubes and graphene save stability under comparative high doses of irradiation [6–8]. Therefore it is very important to know level of stability and understand processes of defect formation in pure polyamide film under irradiation,

The aim of this paper is study changes of electron and vibration properties under influence of high energetic electron irradiation for fluorine-containing polymer PA-24 that is characterised by good thermal and mechanical properties [9].

MATERAILS AND METHODS

Structural formulae of elementary part of fluorine-containing polyamide consists from two phenolic rings that are linked by -OC, -CONH, -NH-groups,



and contains OCF_2CF_2H branch.

Fluorine containing polyamide films were prepared by spin coating from the dimethylformamide solution. Thickness of the film was $d = 1000$ nm. After measurements of the properties in the initial state the film was irradiated with electrons, energy of which was E = 1.8 MeV; doses of the irradiation varied from 1 to 3 MGy. Optical absorption spectra were measured with Shimadzu UV-3100 spectrophotomer, vibration spectra were received with help of Yobin Yvon T64000 microspectrometer λ_{exc} = 532 nm, IR absorption spectra received with help of Nicolet iS50.

In order to receive characteristics of the electron transitions we applied quantum-chemical calculations for the elementary part of fluorine-containing polymer. On the first stage optimization of the geometry with DFT(B3LYP/6-31G, *d*, *p*) was performed and Raman and IR-absorption spectra received. On the second stage for calculations of the electron transitions characteristics of spectra we applied TD SCF method. Typically, calculated and experimental data do not coincide perfectly in quantum-chemical studies [10–12]; however the calculation is precise enough to correctly analyze the nature of electron transitions.

RESULTS AND DISCUSSION

Fig. 1 shows absorption spectra for polyamide film in the initial state (curve 1) and after electron irradiation with doses 1 (curve 2) and 3 MGy (curve 3).

Nonirradiated polyamide film absorbs in UV region and has a shoulder in visible range intensity of which sharply decreases after 350 nm. Lets consider results of quantum-chemical calculations in order to explain the absorption spectrum.

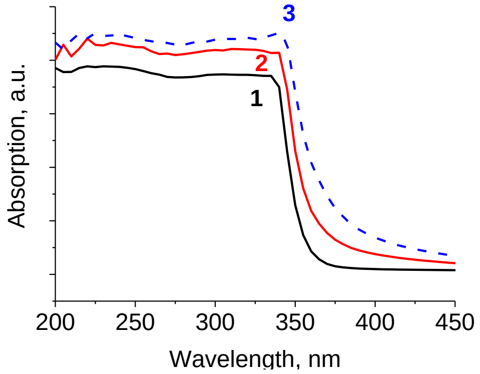


Fig. 1. Absorption spectra for polyamide film in the initial state (curve 1) and after electron irradiation with doses 1 (curve 2) and 3 MGy (curve 3). (Thickness d = 1000 nm, energy of electrons E= 140 keV)

Forms of frontier molecular orbitals and their energies for the polyamide elementary part are represented on Fig. 2. The highest molecular orbital HOMO has energy -6.7 eV, lowest unoccupied molecular orbital LUMO -0.72 eV, energy gap is 6 eV.

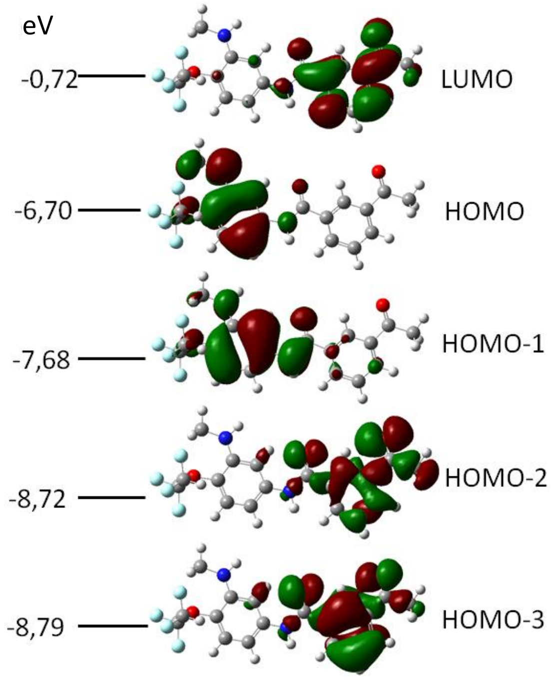


Fig. 2. Energies and forms of frontier molecular orbitals of elementary part of polyamide

As can be seen from Fig. 2, the frontier molecular orbitals are localized on the phenol rings and partially include electron density from oxygen atoms. Maximal oscillator strength *f* and therefore the most intensive transition in the absorption spectrum according to the calculations, Table, is realized due to transition of electron rom HOMO-1 to LUMO level. Calculated wavelength of the transition is 511 nm and differs from the experimental data that is caused by few factors: the first one is consideration of polymer part without taking into account interaction with neighbor parts of polyamide; the second one is calculation of the molecule in vacuum.

Electron transitions of elementary polyamide part near energetic gap

Transition	λ, nm	*f*	Type of transition	Main configuration
$S_0 \rightarrow S_1$	511	1.4	$\pi \rightarrow \pi^*$	HOMO-1→LUMO
$S_0 \rightarrow S_2$	355	0.1	$\pi \rightarrow \pi^*$	HOMO →LUMO
$S_0 \rightarrow S_3$	306	0.5	$\pi \rightarrow \pi^*$	HOMO-4→LUMO

Higher excited states are in better agreement with experiment: wavelength of the second transition $S_0 \rightarrow S_2$ is 355 nm (see Table). Next $S_0 \rightarrow S_3$ transition is at 306 nm and is realized due to transfer of the electron from HOMO-4 on LUMO level. All the transitions are $\pi \rightarrow \pi^*$ type, therefore the calculations classify the fluorine containing polyamide as π-conjugated structure.

Experimental absorption spectra in visible range are not sensitive to irradiation at doses of 1 and 3 MGy, all the maximums save positions and intensities.

Despite of that Raman spectra undergo essential changes. At first let's consider spectrum in the initial stage. As the calculations show (Fig. 3), Raman spectrum has row of vibrational bands in the region 1200…1720 cm^{-1}, and vibrations within 2980…3150 cm^{-1}.

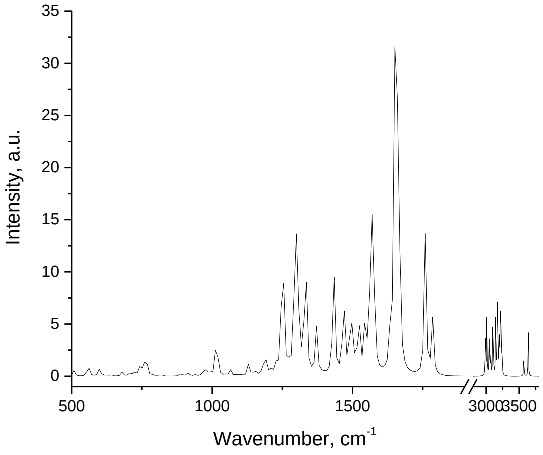
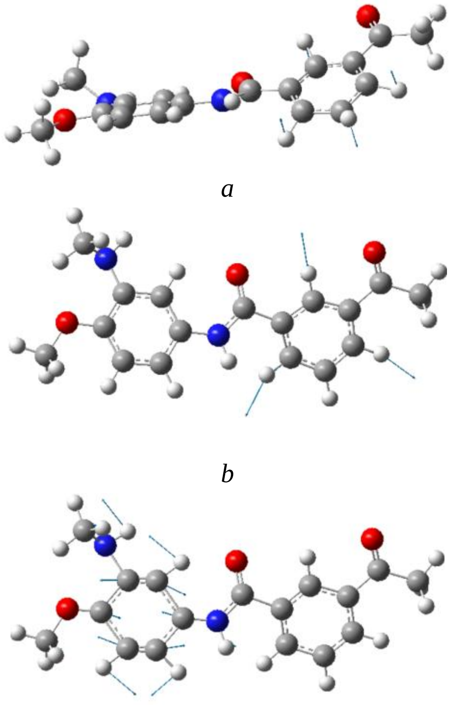


Fig. 3. Calculated Raman spectrum for elementary part of polyamide

Positions of the calculated bands are in good agreement with the experimental ones (Fig. 5, curve 1). For example, low intensive band at 994 cm^{-1}, that in the experiment is at 997 cm^{-1} and has high intensity, corresponds to unsymmetrical bending of phenol ring, Fig. 4,a. Intensities of experimental and calculated vibration bands are different due to abovementioned factors.

The most intensive vibration in the calculated spectrum at 1661 cm^{-1} corresponds to symmetrical breathing of phenol ring, Fig. 4,b. Unsymmetrical shift of phenol ring that includes shift of Nitrogen atom at 1015 cm^{-1} is presented on Fig. 4,c.



a

b

c

Fig. 4. Forms of vibrations of elementary part of polyamide at 994 (a); 1015 (b); 1661 (c) cm^{-1}. Arrows show directions of atomic displacements

Electron irradiation at dose 1 MGy of polyamide film causes slight change of vibration bands form and redistribution of their intensities. Shit of the bends is not observed but some background in the region 2500…3500 cm^{-1}, appears. Irradiation with 3 MGy leads to growing of the background starting from 500 cm^{-1}.

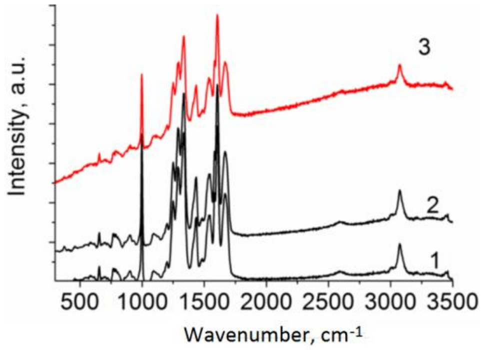


Fig. 5. Raman spectra of fluorine containing polyamide in the initial state (curve 1) and after irradiation with electrons 1 MGy (curve 2), 3 MGy (curve 3). (Thickness of the film d = 1000 nm, energy of electrons E = 1.8 MeV)

Decrease of the intensities of bands at 2550 cm^{-1}, shift of mode at 3074 cm^{-1} in high frequency region by 5 cm^{-1} at 3 MGy points on appearance of radiation defects in the film: knocked atoms, broken bonds.

Dose dependences if infrared absorption spectra confirm destruction of the film. In the initial state polyamide is characterized by rich spectrum of vibration bands (Fig. 6, curve 1) and is in good agreement with the calculations, Fig 7.

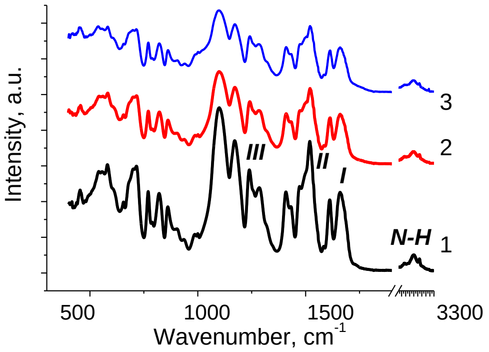


Fig. 6. IR absorption spectra of fluorine containing polyamide in the initial state (curve 1) and after irradiation with electrons 1 MGy (curve 2), 3 MGy (curve 3). (Thickness of the film d = 1000 nm, energy of electrons E= 1.8 MeV)

Similar to the calculations of Raman spectra, intensities in the IR spectrum do not coincide with the experimental ones but positions of vibrations are in agreement.

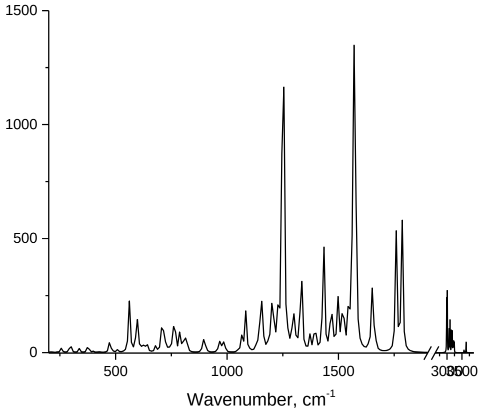


Fig. 7. Calculated IR-absorption spectrum for elementary part of polyamide

In the initial state of fluorine-containing polyamide IR-absorption spectrum have vibrations of amide groups at 1660, 1540, 1230 cm^{-1}, and vibrations of N-H bonds at 3300 cm^{-1}. It should be noted that vibrations of hydrogen bonds are revealed both in Raman and IR spectra in region 3000…3100 cm^{-1}.

Electron irradiation results in significant transformation of the spectra, for example, mode at 1096 cm^{-1} shifts to 1100 cm^{-1} at 1 MGy and to 1105 cm^{-1} at 3 MGy. For the vibration mode at 1661 cm^{-1} no shift is observed at the applied doses but its intensity decreases. Similar to dose dependences of Raman spectra for polyamide, it is observed fall of vibrational intensities in IR-absorption spectra. The fall is caused by breaking of chemical bonds in the polymer, background is due to appearance of great amount of knocked atoms in the structure of the film.

CONCLUSIONS

Influence of high energetic electron irradiation (E_i = 1.8 MeV) on the electron and vibrational properties of fluorine containing polyamide films was studied. Nature of electron transitions and vibration bands in Raman and IR-absorption spectra in the initial

state of the film was determined by quantum-chemical calculations. It is shown that fluorine-containing polyamide PA-24 is π-conjugated system absorption in which is caused by electron transitions between molecular orbitals localized on phenol rings. Results of optical absorption, Raman scattering and IR-absorption showed that irradiation of the film with dose of 1 MGy does not lead to significant changes of electron and vibrational structure. Increase of the dose to 3 MGy influences the intensity of vibration bands in Raman and IR-absorption spectra. Films that were transparent in the initial state became yellow-colored and fragile after the irradiation.

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Статья поступила в редакцию 12.06.2017 г.

ЭЛЕКТРОННАЯ И КОЛЕБАТЕЛЬНАЯ СТРУКТУРА ПЛЕНОК ФТОРСОДЕРЖАЩЕГО ПОЛИАМИДА ПРИ ОБЛУЧЕНИИ ВЫСОКОЭНЕРГЕТИЧЕСКИМИ ЭЛЕКТРОНАМИ

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Приведены исследования влияния облучения пленок фторсодержащего полиамида высокоэнергетическими электронами (E_i = 1,8 МэВ) на его электронную и колебательную структуру. С помощью квантово-химических расчетов установлена природа электронных переходов и полос КРС, а также ИК-поглощения в исходном состоянии. Результаты оптического и ИК-поглощения, рамановского рассеяния света показывают, что данные пленки при дозе 1 МГр сохраняют свою электронную и колебательную структуру. Увеличение дозы до 3 МГр приводит к изменению интенсивностей колеблющихся мод в спектрах рамановского рассеяния и ИК-поглощения. При данной дозе пленки теряют прозрачность, приобретая желтый цвет, и становятся хрупкими.

ЕЛЕКТРОННА ТА КОЛИВНА СТРУКТУРА ФТОРВМІСНОГО ПОЛІАМІДУ ПРИ ОПРОМІНЕННІ ВИСОКОЕНЕРГЕТИЧНИМИ ЕЛЕКТРОНАМИ

О.Л. Павленко, В.А. Сендюк, О.П. Дмитренко, М.П. Куліш, Є.В. Шелудько, О.Д. Качковський, О.О. Ільченко, В.В. Шлапацька

Приведено дослідження впливу опромінення плівок фторвмісного поліаміду високоенергетичними електронами (E_i = 1,8 МеВ) на його електронну та коливну структуру. За допомогою квантово-хімічних розрахунків встановлено природу електронних переходів та смуг КРС, а також ІЧ-поглинання у вихідному стані. Результати оптичного та ІЧ-поглинаннь, раманівського розсіяння світла показують, що дані плівки при дозі 1 МГр зберігають свою електронну та коливну структуру. Збільшення дози до 3 МГр призводить до зміни інтенсивностей коливних мод у спектрах раманівського розсіяння та ІЧ-поглинання. При даній дозі плівки втрачають прозорість, набуваючи жовтого кольору, і стають крихкими.