Electron-conformational rearrangement in nanocomposites films of poly-N-epoxypropylcarbazole with fullerenes C_{60}

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Optical absorption spectra, optical conductivity, refractive index n, extinction coefficient k and photoluminescence in nanocomposite films of poly-N-epoxypropylcarbazole (PEPC) with 0,7; 1,35; 2,5 and 4 wt.% of C_{60} molecules were studied. Substantial restructuring of these spectra with changing the fullerene C_{60} content was established not only in the intrinsic absorption, but also within the energy gap. Reducing the energy distance between states S_1 and T_1 with increasing concentration of C_{60} molecules was showed, as well as the appearance of additional broad structureless bands with a maximum near 700 nm in the long-wave photoluminescence spectrum. Restructuring of the spectra is associated with electron-conformational changes caused by appearance of the donor-acceptor interaction between components in the films PEPC-C_{60} due to formation of the complexes with charge transfer (CCT) in them.

Keywords: nanocomposites, poly-N-epoxypropylcarbazole, C_{60} fullerenes, optical conductivity, optical absorption, photoluminescence, complexes with charge transfer.

Исследованы спектры оптического поглощения, оптической проводимости, показателя преломления n, коэффициента экстинкции k и фотолюминесценции в пленках нанокомпозитов поли-N-эпоксипропилкарбазола (ПЭПК) с 0,7; 1,35; 2,5 и 4 мас.% молекул C_{60}. Установлено существенную перестройку указанных спектров с изменением содержания фуллеренов C_{60} не только в области собственного поглощения, а также в пределах энергетической щели. Показано уменьшение энергетического расстояния между состояниями S_1 и T_1 с ростом концентрации молекул C_{60}, а также возникновение в длинноволновой области спектра фотолюминесценции дополнительных широких бесструктурных полос с максимумом около 700 нм. Перестройка спектров связывается с электрон-конформационными изменениями, вызванными появлением в пленках нанокомпозитов ПЭПК-C_{60} донорно-акцепторного взаимодействия между компонентами в результате формирования в них комплексов с переносом зарядов.

Електронно-конформаційна перебудова у плівках нанокомпозитів полі-N-епоксипропілкарбазолу з фулеренами C_{60}. *О.П.Оласюк, О.П.Дмитренко, М.П.Куліш, М.А.Заболотний, Г.Ю.Бородіна, Т.О.Буско.*

Досліджено спектри оптичного поглинання, оптичної провідності, показника заломлення n, коефіцієнта екстинкції k та фотолюмінесценції у плівках нанокомпозитів полі-N-епоксипропілкарбазолу (ПЕПК) з 0,7; 1,35; 2,5 і 4 мас.% молекул C_{60}. Встановлено суттєву перебудову вказаних спектрів зі зміною вмісту фулеренів C_{60} не лише в

області власного поглинання, а також у межах енергетичної щілини. Показано зменшення енергетичної відстані між станами S_1 і T_1 зі зростанням концентрації молекул C_{60}, а також виникнення у довгохвильовій області спектра фотолюмінесценції додаткових широких безструктурних смуг з максимумом біля 700 нм. Перебудова спектрів зв'язується з електрон-конформаційними змінами, викликаними появою в плівках нанокомпозитів ПЕПК-C_{60} донорно-акцепторної взаємодії між компонентами внаслідок формування у них комплексів із перенесенням зарядів.

1. Introduction

Conjugated polymers with linear or phenyl π-systems in main chain (and in side groups) cause considerable interest as promising lead materials. Among others, there are polymers of poly-N-vinylcarbazole (PVC), poly-N-epoxypropylcarbazole (PEPC), those contain carbazole fragments in the side groups, Fig. 1(a, b).

Despite presence of the same carbazole rings that act as chromophore groups in the molecular structure of the monomer units of these polymers, their structure is different. PVC refers to hard chain polymers in viniline row and PEPC — to polyether oligomers.

These polymers are characterized by semiconducting properties due to the presence of carbazole cores in their structure, which define by the delocalized π-electrons and dipole-dipole interaction and, as a consequent, transfer of energy by excitons and photoconductivity. As a result, such polymers that contain carbazole are widely used for the manufacturing of recording media, high contrasting light emitting devices and low-cost organic solar cells [1, 2].

However, the longer monomer units due to the presence of an oxygen atom and the presence of side bond specified by CH_2 group leads to the fact that carbazole cores haven't fixed positions in PEPC (unlike PVC), and the distances between them are more significant. These differences prevent creation of intramolecular excimers in PEPC and therefore their light sensitivity is insufficient. Sensitizing additives are doped in the polymer matrix for its increase, through which there are created not only more effective photogeneration centers, but also charge carriers and excitons transport are provided [3–5].

One of the sensitization internal photoeffect methods is doping the organic semiconductors by molecules with a high electron affinity energy, which may contribute to the donor-acceptor complexes with charge transfer (CCT) and related optical absorption band appearance. Such heterogeneous systems (under certain conditions) can not only photogenerate exciton like electron-hole pairs (EHP) of carriers, but also effective dissociate and transport them in the electric field.

Especially promising acceptors in the matrixes with polymers that contain carbazole, chromophore molecules, and that have low ionization potential, and therefore can be electron donors, are fullerenes C_{60}. Their electron affinity energy is equal to 2.65 eV [6]. Because of icosahedral symmetry of molecules C_{60}, which provides high tunneling electron transitions probability. Addition of the fullerenes not only provides the efficient EHP formation, but also creates an additional channel for electron transport, which reduces the bulk charge due to the increased charge carriers mobility [7–13]. An important role is plaid not only by bulk arrangement of anisotropic elements with π-orbitals, but also by macroscopic bulk alignment of the polymer chains, which can be achieved in one active layer of organic solar cells (OSC) with bulk heterojunction, when polymer that contains carbazole as a donor and molecule C_{60} as an acceptors form the interpenetrating network for efficient charge separation [14]. Indicated nanostructure (for the effectively work OSC) must have a size corresponding to exciton diffusion length, which is provided their movement and dissociation to electron and hole without radiative recombination [15].

It should be noted that studies of the field impact on behavior of the electron-conformational states of nanocomposites PEPC with fullerene C_{60}, which can be used to create OSC with the bulk heterojunction, not done enough at present.

In this paper, we investigated optical absorption and optical parameters such as refractive index n, extinction coefficient k, optical conductivity σ, photoluminescence for studying properties of PEPC films with different content of molecules C_{60}.

2. Experimental

PEPC films with C_{60} fullerenes were produced by irrigation. The polymer and fullerenes solutions in toluene were previously obtained for this purpose. Concentration of

molecules C_{60} in the solutions was 0; 0.7; 1.35; 2.5 and 4.0 wt.%. Then these solutions were poured on quartz and silicon Si(100) substrate and dried in a thermocell at temperature of 80°C for 4 h. The film thickness d was assumed about 1 μm.

Optical absorption was measured by a spectrometer Perkin Elmer Lambda 35. Optical parameters n and k and optical conductivity σ were determined by using spectral ellipsometry method with the device LEF-ZM-1.

Photoluminescence was studied by using two-beam spectrometer DFS-24 with monochromator MDR-3 and triple electrometer Horbia Jobin Yvon T64000, equipped with a cooled CCD-detector. Spectra were excited by Ar-Krion laser lines with wavelengths 448 and 514.5 nm, and nitrogen laser with wavelength 337.1 and 325 nm.

The films structure determined by X-ray diffractometer DRON-3M with monochromatic radiation of $CoK_{(\alpha1,2)}$ (λ = 0.179021 nm).

3. Results and discussion

Fig. 1(c) shows spectrum of optical conductivity for thin PEPC film.

It shows that for this PEPC film thickness there are observed interference bands in the energy range from 1.5 to 3.4 eV, which presence enables to calculate the value of d for it by using the following expression:

$$d = \frac{1}{2n\left(\dfrac{1}{\lambda_2} - \dfrac{1}{\lambda_1}\right)\sin\varphi}, \qquad (1)$$

where λ_1 and λ_2 — wavelengths of two adjacent interference maxima, n — refractive index, φ — angle of light incidence. The calculation results show that the film thickness is about 1.2 μm, which is consistent with the predictable film thickness. However, it is clear that it must be used a film of greater thickness for ellipsometric measurements to avoid the appearance of interference spectra in the whole energy range of incident photons.

There is no crystal structure for all the PEPC films, as it is evident from the behavior of X-ray diffraction spectrum in the range of angles from 5 to 40 degrees.

Only blurred halo is observed in the X-ray diffraction spectrum that indicates the amorphous structure of PEPC films, which is characteristic for oligomers with low molecular weight, Fig. 1(d).

It is known from optical absorption and fluorescence excitation spectra for PEPC films, that they are mainly derived by energy states, which are characteristic for their monomer polymers units [16].

Fig. 1(e) shows the optical absorption spectrum in the intrinsic absorption area of the monomer units for the PEPC film.

It can be seen that the optical absorption edge corresponds to about 3.55 eV and there is characteristic presence of four clearly expressed bands that due to the singlet energy states S_1–S_4 and single band corresponding to the triplet state T_1. Thus, the absorption maxima corresponding to the optical transitions in the monomer units are associated with excitation of singlet and triplet excitons.

However, there are bands in the optical absorption spectrum as in the optical conductivity, Fig. 1(f), due to the interorbital transitions outside the intrinsic absorption in the range of energies 3.0–1.0 eV. There are 12 bands in the optical absorption spectra in the energy range from 3.6 to 1.0 eV, which absorption coefficient decreases in 10^3–10^5 times in comparison with the intrinsic absorption bands.

It is seen that there are individual bands of the optical conductivity with the small energy to the absorption edge, their value is less than $0.5 \cdot 10^{15}$ s^{-1}. This indicates the existence of local states within the energy gap that results from the formation of various complexes, photooxide of carbazole rings, as well as the existence of molecular adulterants.

It should be noted that the addition of acceptor molecules C_{60} in the PEPC matrix does not change general view of the optical conductivity spectrum, where the singlet and triplet states are saved, that is characteristic for the polymer monomer units, Fig. 2.

However, depending on the content of fullerenes the position and relative intensity of bands S_1–S_4 and T_1 are changed. Thus, optical transitions in the triplet T_1 (4.11 eV) and singlet S_1 (4.52 eV) states are clearly expressed in the PEPC optical conductivity spectrum. S_1 (4.65 eV) and S_3 (5.01 eV) transitions are displaced from their positions in the PEPC nanocomposites with 0.7 wt.% C_{60}, and S_2 transition, corresponding to 4.84 eV of energy, is hardly evident. In addition, a value redistribution of optical conductivity occurs for some bands.

Optical conductivity spectrum changes are more significant in the intrinsic absorption area in the case of increase of C_{60}
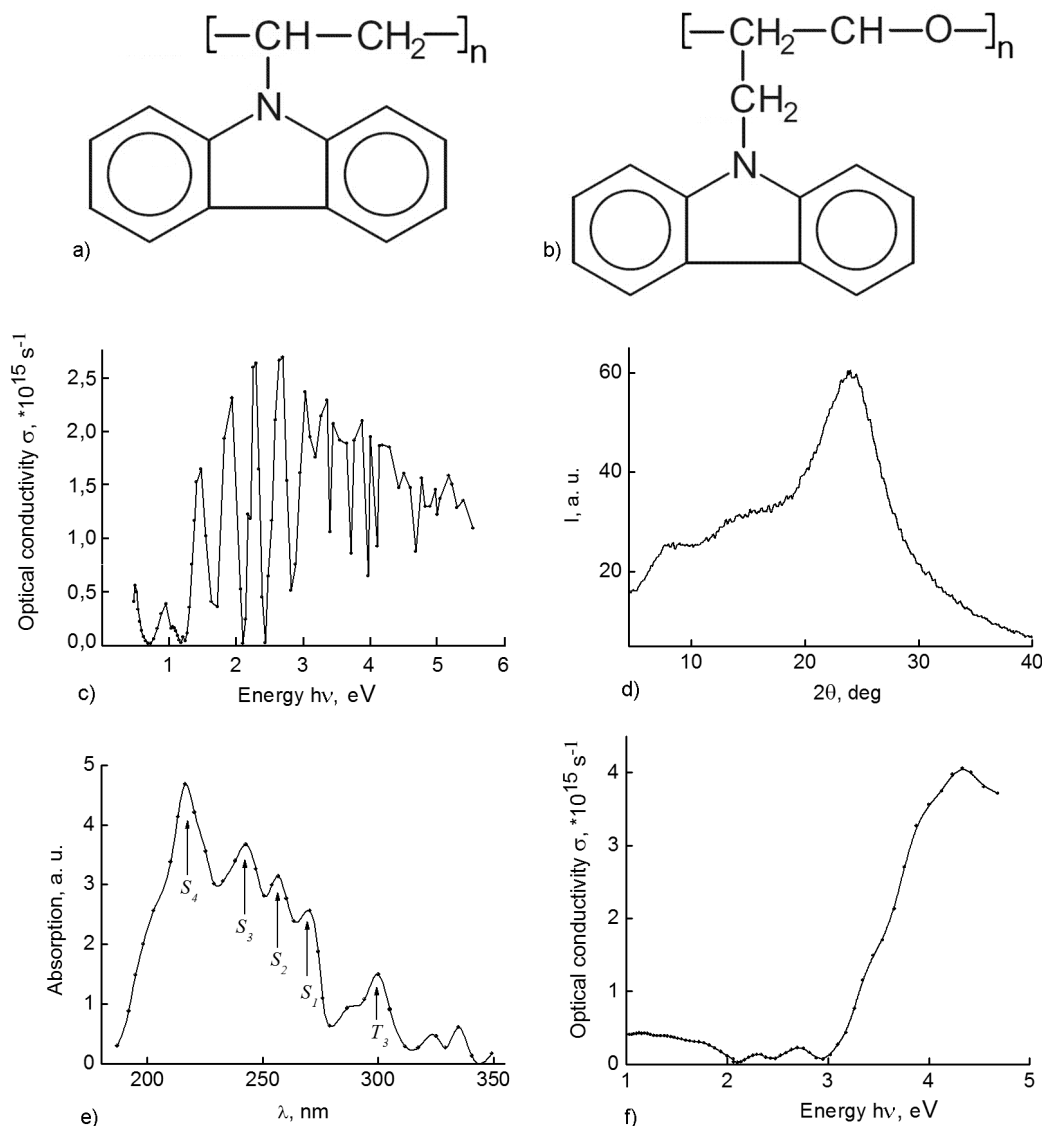
Fig. 1. Structures of PVC (a) and PEPC (b) and PEPC film; optical conductivity spectrum of thin film (c), X-ray diffraction spectrum ($\lambda_{CoK\alpha} = 0.179021$ nm) (d), optical absorption spectrum in intrinsic absorption region (e), optical conductivity spectrum ($d = 2$ μm) (f).

molecules to 1,35 wt.%. If the bands T_1 (4.12 eV) and S_1 (4.59 eV) save their position, then the place of other optical conductivity peaks changes. Additional bands appear in the spectrum. Importantly, that it is a significant redistribution of absorption intensity for all maxima σ due to falling of the optical conductivity value for the low energy range in the spectra for PEPC compared with its nanocomposite with 0.7 wt.% of C_{60}. A similar spectrum restructuring continues in the case of increased concentration of C_{60} to 2.5 wt.% in nanocomposite. T_1 peak position is significantly shifts to the energy value of 4.21 eV for this system, the maximum near 4.59 eV almost disappears, and the other peaks are shifted and demonstrate significant changes in intensity.

The biggest restructuring of σ spectrum occurs for PEPC nanocomposite with 4.0 wt.% C_{60}. Thus, the line for the triplet transition T_1 almost disappears, but an additional band appears at 4.30 eV. It can be assumed that doping the polymer by fullerenes C_{60} reduces the energy gap between the states S_1 and T_1, a tendency to that is viewed in the case of nanocomposite with 2.5 wt.% of C_{60}. S_4 band at 5.71 eV is shifted to the position on 5.21 eV. The greatest absorption in this range occurs for band S_3 (5.03 eV).
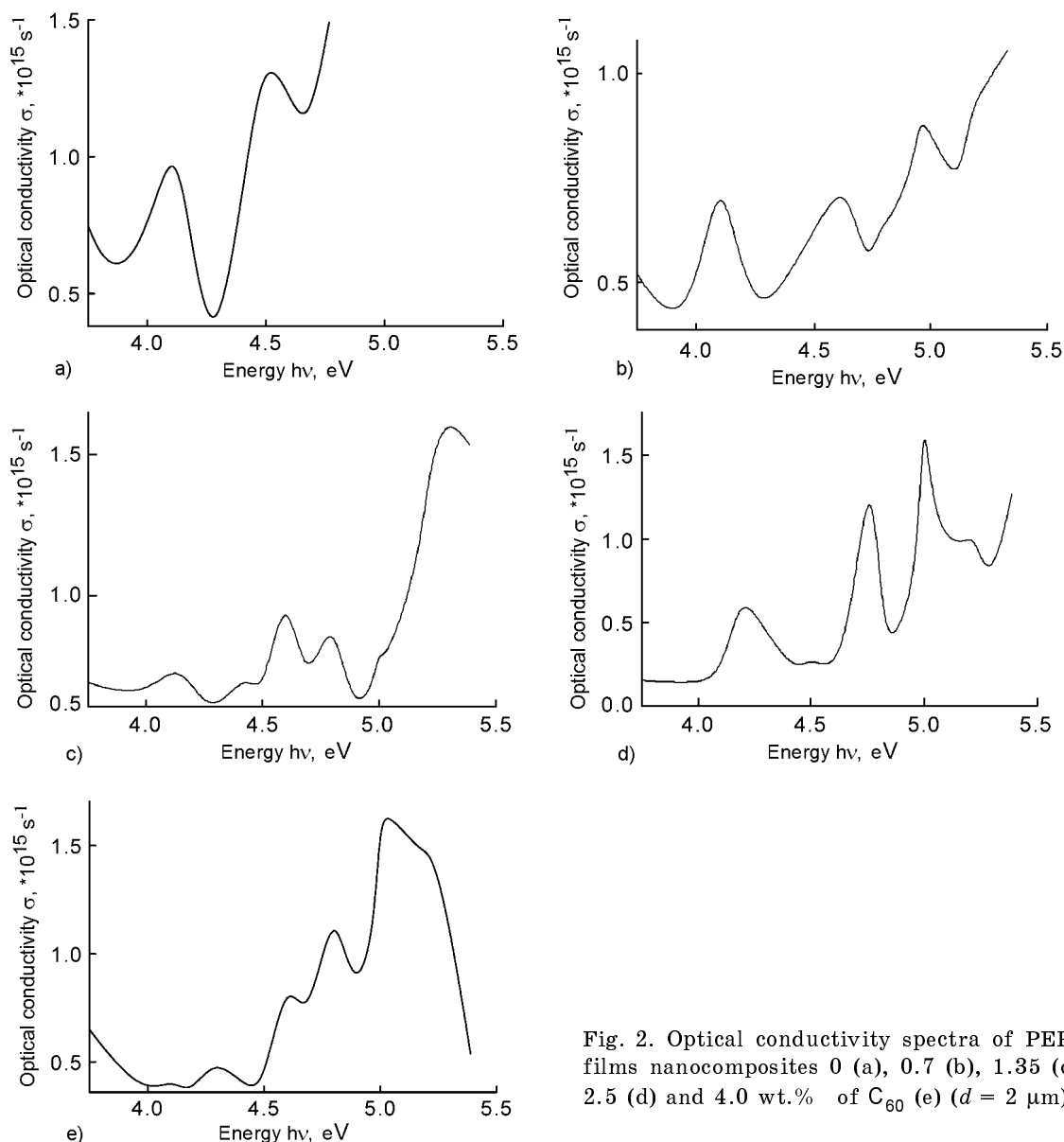
Fig. 2. Optical conductivity spectra of PEPC films nanocomposites 0 (a), 0.7 (b), 1.35 (c), 2.5 (d) and 4.0 wt.% of C_{60} (e) ($d = 2$ μm).

Thus, the spectra of optical conductivity for the PEPC nanocomposites with different content of C_{60} molecules undergo significant changes. These spectra restructuring of the PEPC monomer units is a result of appearance of donor-acceptor interaction between the components of nanocomposites, which leads to CCT formation. Dynamics of the CCT production become complicated with the changing the C_{60} content, since their homogeneous distribution in the matrix can be expected only for the low concentrations of fullerenes and growth for the molecules content increases their aggregation probability that prevents appearance of the donor-acceptor complexes. The role of C_{60} molecules in reducing the distance between S_1 and T_1 states in the monomer units is especially significant, which can make an important contribution to the growth of intercombination transitions and, consequently, in the strengthening of the donor-acceptor interaction.

Refractive index n and extinction coefficient k spectra are also changed, Fig. 3.

It is evident that the both optical parameters significantly change with the change of the C_{60} molecules content in nanocomposites with PEPC not only in the range of smaller as well as in the larger wavelengths. This spectra restructuring also indicates the formation of CCT in the PEPC nanocomposites with C_{60}, which leads to a the spectra restructuring of not only in the intrinsic absorption area, but also within the energy gap. It becomes especially notice-
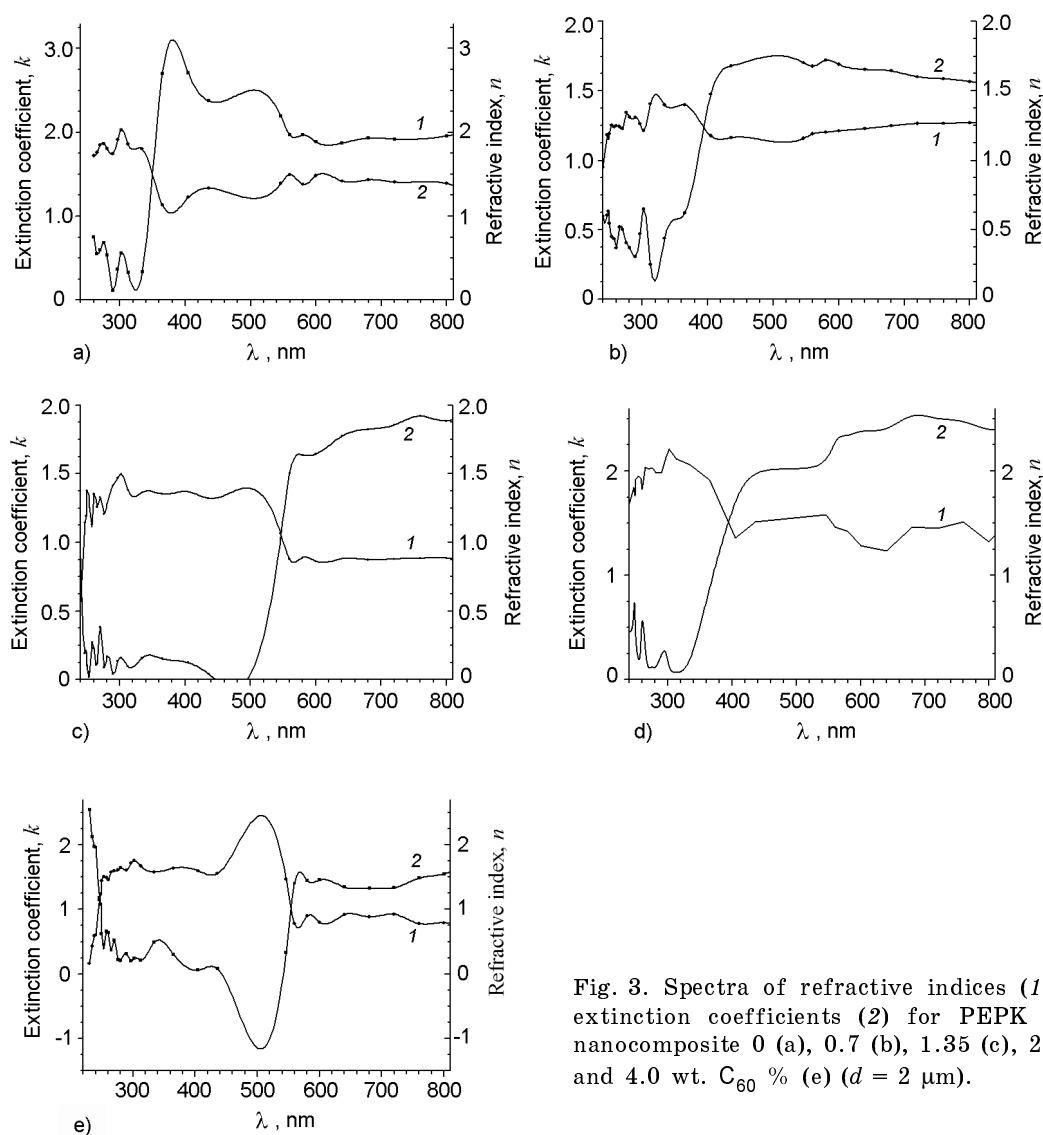
Fig. 3. Spectra of refractive indices (*1*) and extinction coefficients (*2*) for PEPK films nanocomposite 0 (a), 0.7 (b), 1.35 (c), 2.5 (d) and 4.0 wt. C_{60} % (e) (d = 2 μm).

able in the area after 500 nm, which corresponds to a the wavelength band of charge transfer which is close to 590 nm.

Photoluminescence spectra, which reproduces the dynamics of relaxation processes of electronic excitations for the PEPC films (including the case of substitution of hydrogen atoms for carbazole fragments), are quite complex [16–18]. The entire range of wavelengths can be divided into several sections. There are three bands at 350, 367 and 386 nm in the range of wavelengths λ < 400 nm for stationary photoluminescence, corresponding to radiation due to relaxation of electronic excitations in π-system of the carbazole fragments. If the band at 350 nm is associated with O–O electronic transfer, the last two bands are due to vibronic transitions. Phosphorescence spectrum (FS) is concentrated in the range of

λ > 400 nm (beside the fluorescence spectrum of monomer units), which includes intense bands at 412 and 441 nm and low-intensity peaks near 425, 431, 456 and 465 nm. Broad structureless bands are observed at 460–480 and 520 nm in addition to given bands in the PL spectra. The nature of the separate bands may vary depending on the PEPC films condition or powder, Fig. 4(a).

The feature of this spectrum is the broad structureless band in the region of 460–650 nm, which includes not only bands at 460–480 and 520 nm, but also indicates the presence of a more long-wave maxima.

The band at 450–460 nm belongs to existence of sandwich type the excimer with almost completely overlapped π-systems. The appearance of the band at 520 nm (2.38 eV) due to formation of photooxides
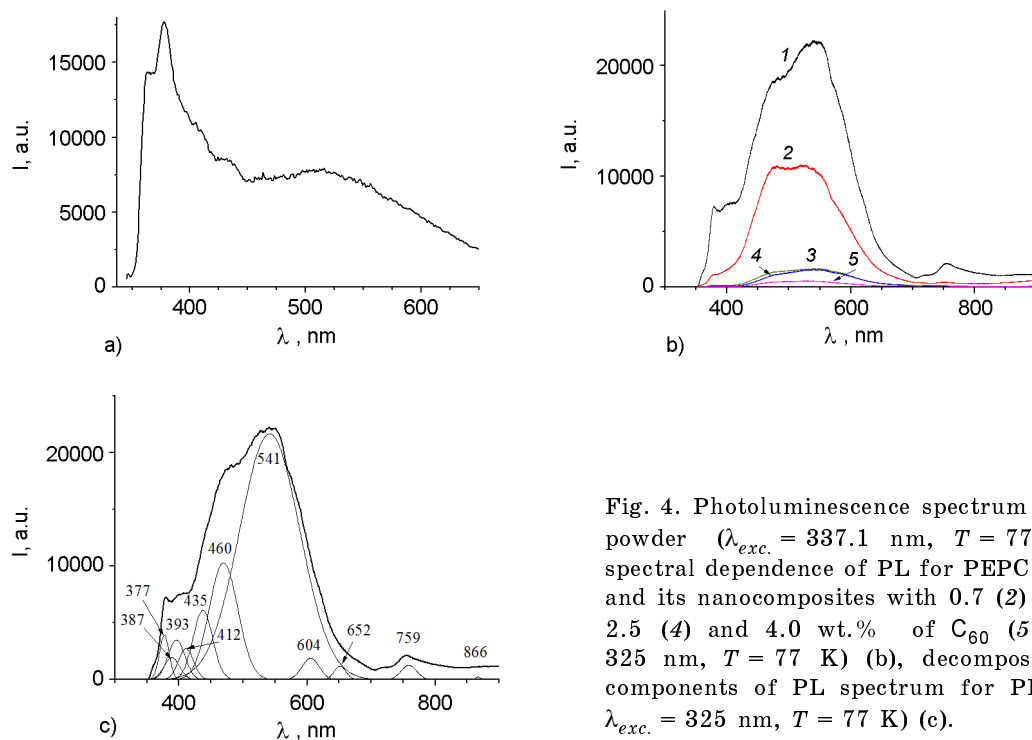
a)

b)

c)

Fig. 4. Photoluminescence spectrum of PEPC powder ($\lambda_{exc.}$ = 337.1 nm, T = 77 K) (a), spectral dependence of PL for PEPC films (*1*) and its nanocomposites with 0.7 (*2*) 1.35 (*3*), 2.5 (*4*) and 4.0 wt.% of C_{60} (*5*) ($\lambda_{exc.}$ = 325 nm, T = 77 K) (b), decomposition for components of PL spectrum for PEPC film $\lambda_{exc.}$ = 325 nm, T = 77 K) (c).

or exciplexphotooxides with normal oxygenless links [18]. By the way, the intensity of the band at 520 nm increases with the temperature growing, which also shows its excimer-exciplex nature. It should be recalled that excimer and exciplex formation (due to the PEPC structural features) unlike PVC occurs due to intermolecular last groups. Also it is possible the radiation in $\lambda > 400$ nm area (in addition to the excimers) by dimer complexes with their local levels in the ground state.

The intensity of the excimer and exciplex bands significantly increases during the light excitation with energy $h\nu$ = 2.1 eV (590 nm) [16]. It should be noted that the existence of the long wave PL can also be due to other causes. Delocalization of triplet excitons at increased temperatures (77 K) generated by monomer units can be as one of such reasons. As a result of T_1-excitons migration they can get into the deep traps which appear on photooxidized centers. The phosphorescence spectrum (due to recombination of these excitons) corresponds to the broad structureless band with a maximum in the vicinity of 500−550 nm [18]. Another reason could be the appearance of CCT with acceptors, including C_{60} molecules, the absorption of which is concentrated in 380−500 nm (2.48−3.26 eV) region. Since it is overlapped with radiation bands of the

monomer units and excimers, it can be expected the secondary absorption (reabsorption), which promotes the resonant energy transfer from these units and excimer CCT, which radiation focuses in the area of 500−850 nm. It is possible that at the initial stage of photooxidation the appearance of exciplexes, T_1-exciton radiation from deep traps that appear due to photooxidation can strengthen the PL as a result of the laying CCT on PL [17]. It is appropriate to consider restructuring of the PL spectra for the PEPC nanocomposites with different content of acceptor molecules C_{60} in the broad structureless band during excitation on different wavelengths to determine the possibilities for flowing of relaxation processes.

Fig. 4(b) shows the normalized spectral dependence PL near wavelength of 550 nm excited by light with wavelength λ = 325 nm obtained for the PEPC and its nanocomposites with molecules C_{60} at temperature T = 77 K.

It is seen that the PL spectrum for the PEPC films is significantly different from analogous spectrum for the polymer powder. When the higher values of PL correspond to the relaxation processes of electronic excitations in the emission area of the monomer units, and there is little intense broad structureless band in the long-wave region for the powder PEPC, then for the films, conversely,
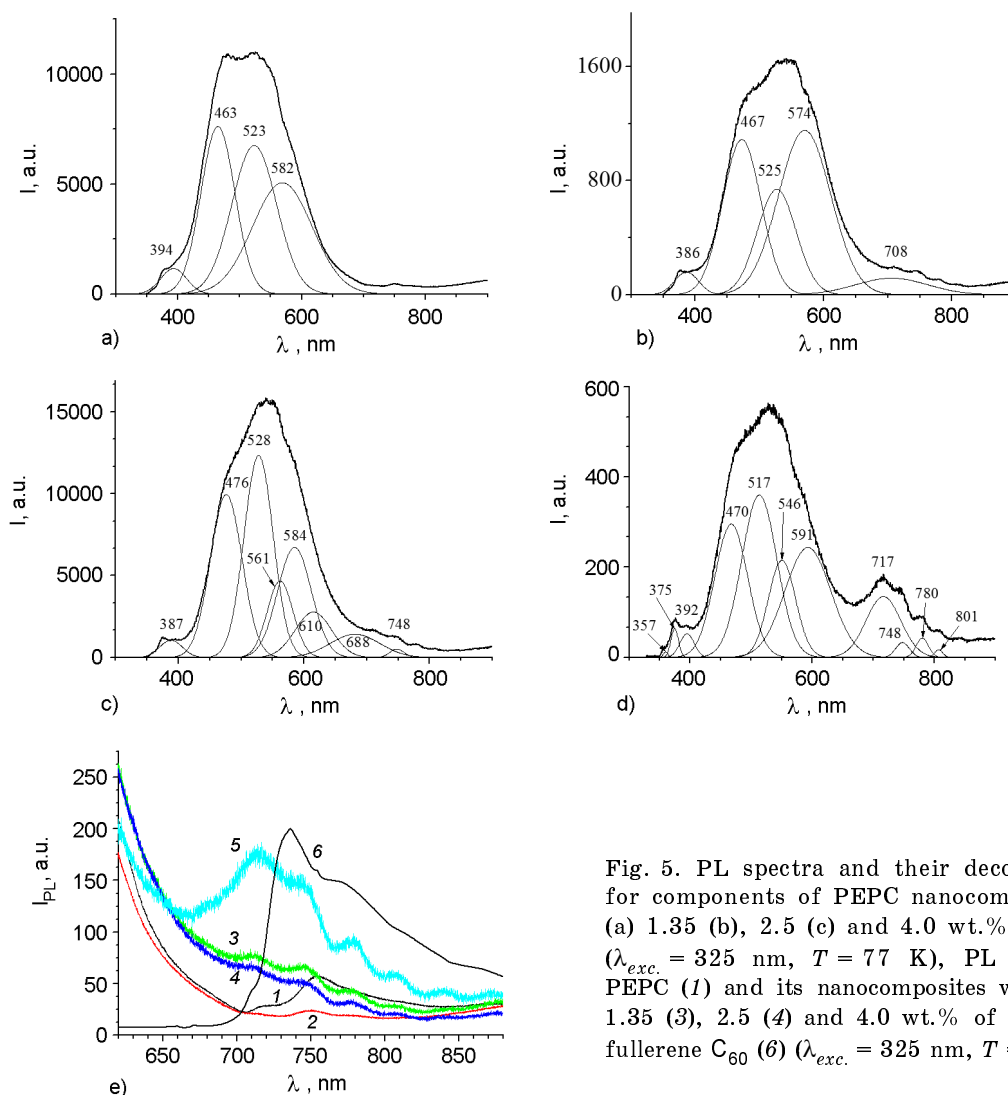
Fig. 5. PL spectra and their decompositions for components of PEPC nanocomposites 0.7 (a) 1.35 (b), 2.5 (c) and 4.0 wt.% of C_{60} (d) ($\lambda_{exc.}$ = 325 nm, T = 77 K), PL spectra of PEPC (*1*) and its nanocomposites with 0.7 (*2*) 1.35 (*3*), 2.5 (*4*) and 4.0 wt.% of C_{60} (*5*) and fullerene C_{60} (*6*) ($\lambda_{exc.}$ = 325 nm, T = 77 K) (e).

bands related to the monomer units, strongly suppressed. However, there is a signif icant radiation in th e range of 400–700 nm, and there is the blurred low-intensity band for PEPC in the range 725–800 nm.

Fig. 4(c) shows decomposition by components of the PL spectrum for the PEPC film measured at a temperature of 77 K.

It is seen that the PL spectrum includes a diverse set of the components that related to the fluorescence (377, 387, 393 nm), phosphorescence (412, 435 nm) on the monomer units, excimer complexes (460 nm), and to T_1-exciton recombination on photooxidized traps. In addition, there is a number of low intensive bands (604, 652, 759, 866 nm), the nature of which is not fully understood, but it can be assumed that they are caused by different nature of the complexes, including photooxidized exciplex. The components distribution and their

relative intensity retain with minor changes for the PL spectra obtained for T = 300 K.

The PL spectra are rebuilt with the addition of C_{60} molecules, but the degree of their changes significantly depends on the fullerenes concentration, Fig. 5(a).

It is seen that already with the small content of C_{60} molecules (0.7 wt.%) there is a significant shift of the bands due to the presence of exciplexes to 523 nm and linked to T_1-exciton recombination on the photooxidized traps to 588 nm. The intensity redistribution is also observed, caused by different relaxation mechanisms of the electronic excitations. It can be assumed that these changes occur as a result of formation of the CCT molecules C_{60} with oxygenless and photooxidized carbazole cores.

The CCT formation is enhanced with increasing the content of C_{60} molecules to 1.35 wt.%, as evidenced by the appearance of additional components of the PL inten-

sity in the long-wave region with a the maximum at 708 nm. The formation of CCT even greater extent continues in the case of increase of the fullerenes concentration. The PL spectra are much more complicated in the long-wave region with presence in the nanocomposites 2.5 and 4.0 wt.% of C_{60}, as a result of radiation by the molecules of C_{60} and CCT.

Fig. 5(b) shows comparison of the PL spectra for fullerenes C_{60} and PEPC nanocomposites with the different content of fullerenes in the long-wave region from 620 to 880 nm.

It is seen that there is the additional emission in the wavelength range between 620 and 690 nm (in which there is no PL that is associated with radiation of fullerene C_{60}), which increases with the concentration of fullerenes. The PL band intensity is approximately the same as in the other components of radiation (for the nanocomposites with 4.0 wt.% C_{60}). Meanwhile, significant contribution to the PL intensity for a given nanocomposite is due to C_{60} molecules in the longer wavelengths. This contribution is much smaller for other nanocomposites. It is obvious that there is focused PL intensity (in the given wavelength range) in addition to radiation by C_{60} molecules, that is generated by the appearance of complexes with charge transfer in the nanocomposites PEPC-C_{60}. It can be assumed that the maximum for the broad band of CCT is close to 700 nm.

Thus, there is dissipation of electronic excitation energy in the PEPC films with C_{60} molecules caused by several mechanisms, which in addition to emissions by the monomer units include the possibility of photoluminescence by the excimer, exiplex complexes, and triplet excitons on the deep photooxidized traps and the CCT of carbazole chromophore π-electron groups with fullerenes C_{60}.

4. Conclusions

There is considerable restructuring of the spectra in the areas of intrinsic absorption and energy gap that can be seen from measurements of optical absorption, optical conductivity, optical parameters n and k for the films of PEPC nanocomposites with 0.7; 1.35; 2.5 and 4.0 wt.% of C_{60}. The restructuring manifests in the shifting of positions of absorption bands, changing their relative intensities, which varies depending on the content of fullerenes C_{60} and defines by concentration of the molecules, and their possibility of aggregation. The distance between the energy states S_1 and T_1 decreases with increasing of content of C_{60} molecules, this plays an important role in strengthening the donor-acceptor interaction.

The PL spectra also undergo changes for these nanocomposites, in which in addition to the bands associated with the monomer units, excimer and exciplex complexes, T_1-exciton recombination on deep photooxidized traps, there are additional structure less broad peaks caused by the CCT occurrence. The bands of charge transfer are characterized by maximum near 700 nm, the magnitude of which increases with the concentration of fullerenes C_{60}.

It is obvious that the occurrence of the PCC increases the quantum yield of geminal electron-hole pairs during the absorption of light in the visible range and improves their dissociations and transport in the relative areas.

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