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OPTICAL PROPERTIES OF CARBON CONTAINING NANOCOMPOSITE FILMS BASED ON THE POLYSTYRENE-FULLERENE C_{60} SYSTEM

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Carbon-based nanocomposites have attracted significant attention due to their unique properties and potential for use in various technological applications. In this study, experimental investigations were conducted to determine the spectral properties of carbon-containing nanocomposite polymer films based on polystyrene (PS) with fullerene C_{60} *nanoadditives. The results indicate that the incorporation of fullerene nanoparticles into the PS matrix enhances the optical properties of the material. Specifically, the optical density of the samples increases, the absorption coefficient increases, and the width of the bandgap decreases with an increase in carbon additive concentration. These findings suggest that fullerene-based nanocomposites are promising materials for optoelectronic and nanotechnological applications. The results of this work contribute to the growing body of research on carbon-based nanocomposites and their potential for use in a range of fields, including electronics, energy storage, and sensing applications. The enhanced optical properties of fullerene-based nanocomposites suggest that they may be particularly useful for developing novel optoelectronic devices and sensors. Overall, this study highlights the potential of fullerene-based nanocomposites as a versatile and promising material platform for various technological applications.*

Keywords: nanocomposite polymer films, carbon nanoparticles, fullerene, polystyrene.

1. Introduction

Fullerene-based materials have recently garnered significant attention from researchers due to their extraordinary properties, which make them an intriguing subject for both fundamental research and practical applications [1-10]. These materials have a broad range of potential applications, including hydrogen storage based on fullerenes in the field of energy [11-13]. Furthermore, fullerene-containing materials have the potential to be utilized for converting solar energy, as well as in drug delivery for medicine [14-17]. Fullerenes' distinctive optical and electrical properties may also make them suitable for creating a foundational basis for microelectronics [18-21].

The considerable interest in carbon nanoparticle-modified polymers stems from the fact that such modifications significantly enhance their physical-chemical properties, including optical, mechanical, and catalytic, while also enabling the acquisition of novel properties such as biological activity [22-24]. These novel nanocomposite polymeric materials with improved physicochemical and operational properties are often adopted to complement or replace conventional materials. Of the various high molecular weight compounds, PS exhibits significant non-covalent binding capacity for fullerene [25-28]. Furthermore, styrene and divinylbenzene copolymers serve as raw materials for producing cationites industrially. Consequently, sorption-active carbon nanoparticle-modified composites based on polystyrene can substantially expand the scope of sorbents while also offering new carbon-containing nanocomposite polymeric materials (films) [29-32]. The objective of this research is to investigate how the inclusion of carbon fullerene C_{60} nanoadditives affects the optical characteristics of the PS-C_{60} matrix.

2. Experimental part. Materials and Research Methods

As is known atactic PS is a stiff amorphous polymer with high optical transparency, low mechanical strength, and low density (1060 kg/m^3). It exhibits dielectric characteristics and is a thermoplastic substance that does not crystallize under external factors [33-35]. However, by introducing various foreign impurities of different activity levels, the structure and physical characteristics can be regulated over a wide range. At present, nanocarbon materials, such as fullerenes and their derivatives, are utilized as modifying additives. The research utilized PS grade 143 E (GOST 20282-743) powder and fullerene C_{60} carbon additives, made in Russia, as the study materials. PS and C_{60} were dissolved in toluene at 20°C, after which a C_{60} solution was added to the PS solution at a specific volume fraction to create a polymer solution blend with fullerene concentrations of C=0, 1, 3, 5, and 10% by weight.

The optical properties of the samples were measured on Cary 60 UV-Vis spectrophotometer (Agilent Technologies), scanning in the wavelength range of 190-1100 nm. An impulse xenon lamp with a dual-beam optical scheme and a Cherni-Turner monochromator is used as the source. Two silicon photodiodes serve as detectors for simultaneous measurement of the light beam of the sample and the reference [36,37].

3. Results and discussion

In this work, the experimental investigation results of the optical properties of the PS-C_{60} system are presented. The absorption spectra *A* of polymer nanocomposites with fullerene carbon additives at different concentrations of C_{60} were measured and analyzed (Fig.1). The absorption spectra *A* of the investigated samples were characterized by significant absorption in the short-wavelength region, which decreased rapidly with increasing wavelength at first and then much more slowly for all samples. The presence of fullerene additives C_{60} in PS led to a significant increase in absorption (curves 2-5, Fig.1), and the absorption further increased with increasing C_{60} concentration up to 10%. The transmittance *T* of PS was found to be 50-62% (curve 1, Fig. 2) and decreased with increasing fullerene concentration from 1 to 10% (Fig. 2).

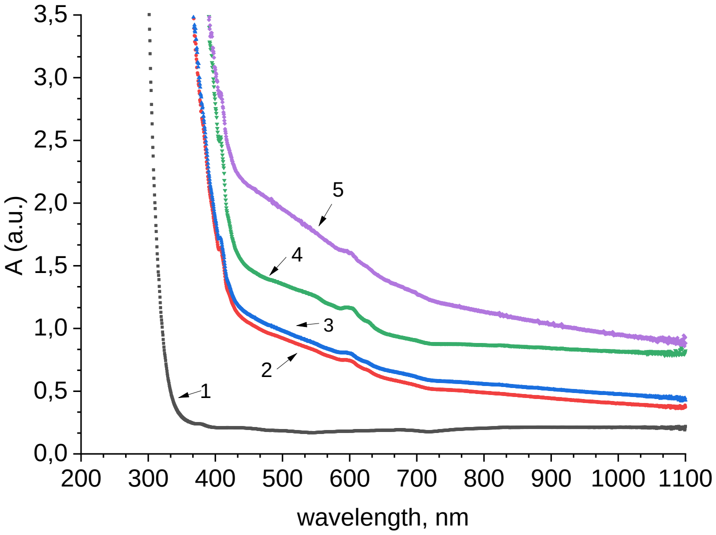

Fig.1. Absorption spectra of PS-C_{60} samples: 1) PS; 2) PS+1% C_{60}; 3) PS+3% C_{60}; 4) PS+5% C_{60}; 5) PS+10% C_{60}.

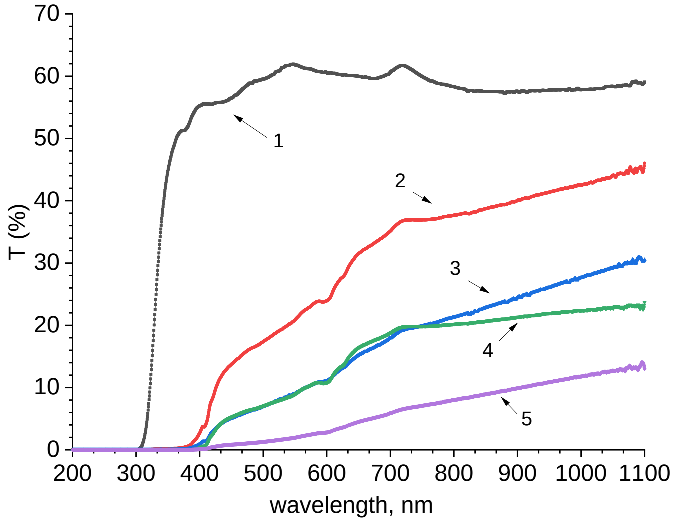

Fig.2. Transmission spectra of PS-C_{60} samples:
1) PS; 2) PS+1% C_{60}; 3) PS+3% C_{60}; 4) PS+5% C_{60}; 5) PS+10% C_{60}.

The dependencies of the reflection spectra R on the wavelength λ for the PS-C_{60} system, presented in Fig. 3, show similar trends to the transmittance spectra T of these samples (Fig. 2), which corresponds to the correlation between the transmittance and reflection of the samples. The value of R for the pure sample is 65-66%, and decreases with increasing concentration of fullerene C_{60}.

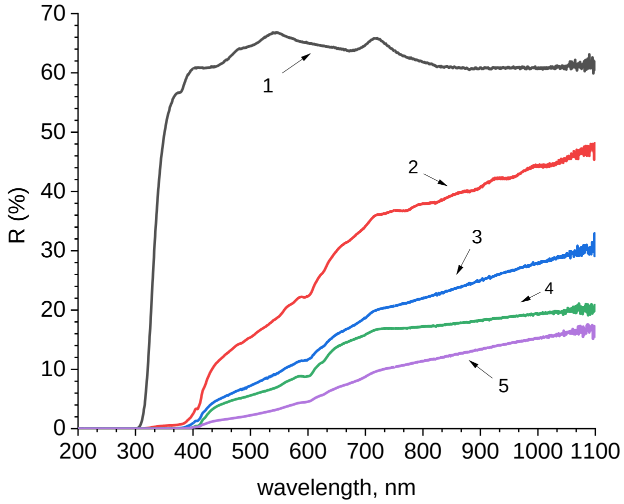

Fig.3. Reflection spectra of PS-C_{60}: 1) PS; 2) PS+1% C_{60}; 3) PS+3% C_{60}; 4) PS+5% C_{60}; 5) PS+10% C_{60}.

Absorption is characterized by the absorption coefficient α, which was calculated using formula:

$$\alpha = 2.303 \cdot \frac{A}{l} \tag{1}$$

where A – absorbtion, l – thickness of the film.

The dependencies of α on the photon energy $h\nu$ at different concentrations are presented in Fig. 4. The value of α gradually increases with increasing photon energy for the pure sample up to energies of 3.56 eV, and then sharply increases. With the addition of C_{60} fullerene to PS, an increase in the absorption coefficient is observed already at energies of approximately 1.13 eV, followed by a region of slight increase in α at energies from 2.02 to 2.11 eV, and at energies of 3.03 eV, a small peak is observed for all C_{60} concentrations (curves 2-5, Fig. 4).

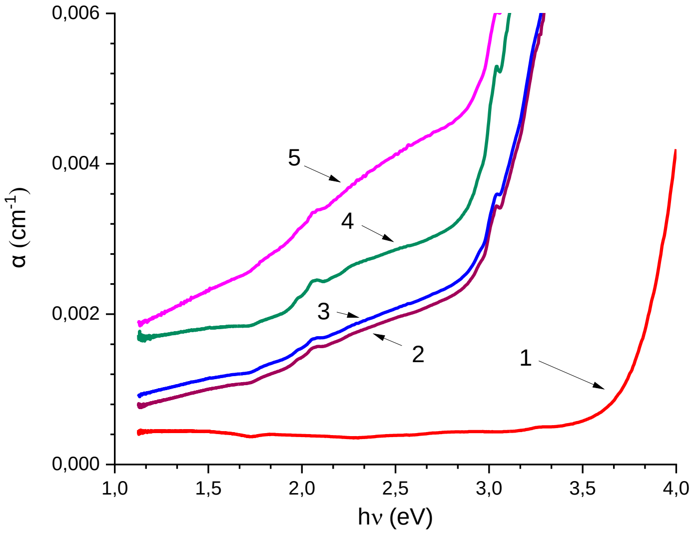

Fig.4. Dependence of the absorption coefficient α on the photon energy $h\nu$ for the PS-C_{60} system at different concentrations of C_{60}: 1) PS; 2) PS+1% C_{60}; 3) PS+3% C_{60}; 4) PS+5% C_{60}; 5) PS+10% C_{60}.

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This indicates a change in the optical properties of the investigated samples with increasing photon energy $h\nu$ and depending on the concentration of fullerene C_{60}. The optical conductivity σ_{opt} of the PS-C_{60} system was also calculated:

$$\sigma_{opt} = \frac{\alpha n c}{4\pi} \qquad (2)$$

where c is the speed of light, n – refractive index.

The graphs of the dependencies of σ_{opt} are shown in Fig. 5. For the PS (curve 1, Fig. 5), the optical conductivity σ_{opt} hardly changes with the increase in $h\nu$ energy. However, the addition of fullerene nanoadditives leads to an increase in σ_{opt} with the increase in photon energy even at low concentrations of C_{60} from (0.524 - 6.696) × 10^9 s^{-1}. A sharp increase in optical conductivity is observed with an increase in the fraction of fullerene (10%) in the PS matrix (curve 5, Fig. 5). This indicates that the addition of fullerene to the PS matrix promotes the enhancement of the optical properties of the PS matrix, namely the optical conductivity.

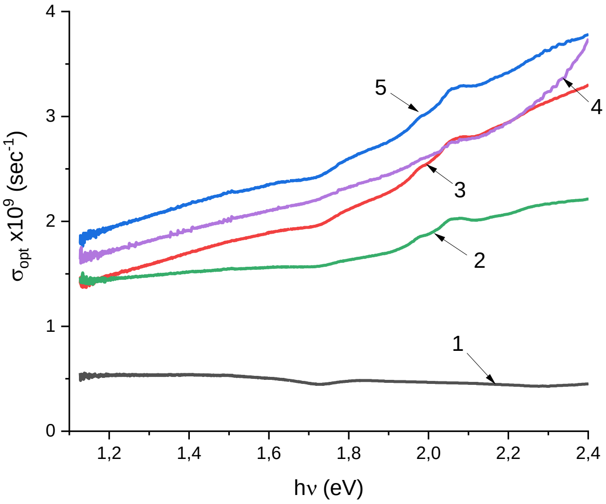
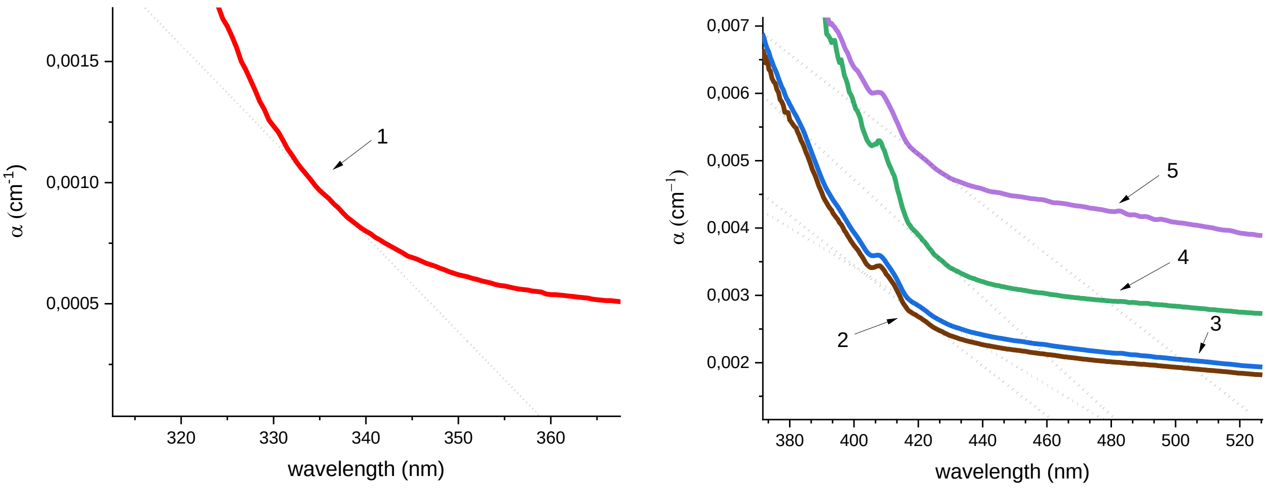


Fig.5. Dependencies of optical conductivity σ_{opt} on the photon energy $h\nu$ for the PS-C_{60} system at different concentrations of C_{60}: 1) PS; 2) PS+1% C_{60}; 3) PS+3% C_{60}; 4) PS+5% C_{60}; 5) PS+10% C_{60}.

To assess the influence of fullerene C_{60} additives on changes in the optical properties of the PS matrix, the absorption edges were determined by extrapolating the steep portions of the curves for the absorption coefficient α (Fig. 6) to the intersection with the x-axis at a certain point. The position of the intersection point gives the value of the optical band edge.



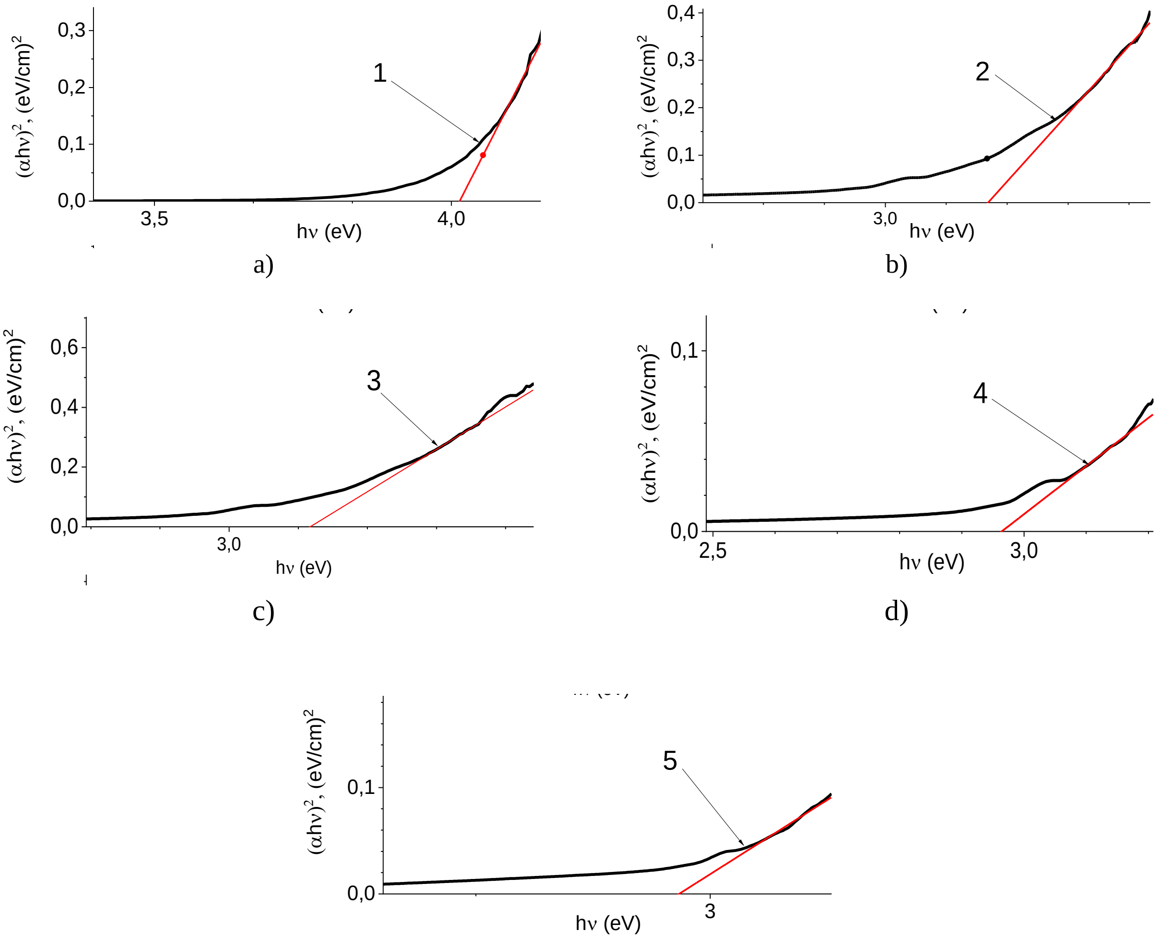
a) b)

Fig.6. Extrapolation of the dependencies of the absorption coefficient α on the photon energy $h\nu$: a): 1) PS; b): 2) PS+1% C_{60}; 3) PS+3% C_{60}; 4) PS+5% C_{60}; 5) PS+10% C_{60}.

The addition of C_{60} fullerene nanoparticles to the PS matrix causes a redshift in the absorption edge, which means that the absorption of light shifts towards longer wavelengths. The intersection points of the curves with the x-axis (as shown in Fig. 6) indicate the position of the absorption edge, which was found to shift towards longer wavelengths with increasing concentration of C_{60} in the PS matrix. The shift in the absorption edge was found to increase from 358 nm for the pure PS sample to 526 nm for the PS+10% C_{60} sample. Material's optical energy band gap E_g is related to its absorption coefficient α and the energy of the incident photon $h\nu$ according to the following equation:

$$(\alpha h\nu)^m = B(h\nu - E_g) \tag{3}$$

where h is the Planck constant, ν is the frequency of the incident radiation, and B and m are constants. The value of m depends on the type of transition between the valence band and the conduction band of the material. The constant m takes on values of 2, 3, 1/2, or 3/2 for allowed direct, forbidden direct, allowed indirect, or forbidden indirect transitions, respectively. Analysis of the absorption spectra of the investigated samples showed that the PS-C_{60} system allows for allowed direct transitions, so the value of m=2 was used in formula (3) to determine the width of the optical band gap E_g. The values of E_g for pure PS and PS with C_{60} fullerene additives at concentrations of 1%, 3%, 5%, and 10% were obtained by extrapolating the linear portions of the $(\alpha h\nu)^2$ curves to the $h\nu$ axis until they intersect with the x-axis. The point of intersection of the curve with the x-axis allows for the determination of E_g (Fig. 7).



a)

b)

c)

d)

e)

Fig.7. Dependence of $(\alpha h\nu)^2$ on $h\nu$ for the studied samples:
1) PS; 2) PS+1% C_{60}; 3) PS+3% C_{60}; 4) PS+5% C_{60}; 5) PS+10% C_{60}.

For clarity, all graphs for pure PS and PS with different concentrations of C_{60} fullerene are presented separately in Fig. 7. The trend of decreasing E_g with increasing percentage of C_{60} fullerene in the PS-C_{60} matrix is clearly visible in Fig. 8, and the addition of just 1% C_{60} leads to a sharp decrease in E_g from 3.972 eV to 1.854 eV (Fig. 8). In other words, increasing the concentration of C_{60} fullerene in the PS matrix leads to a decrease in the width of the optical band gap, which is consistent with the values for the absorption edge wavelength presented in Table 2, where an increase in wavelength is observed with increasing concentration of C_{60} in PS.

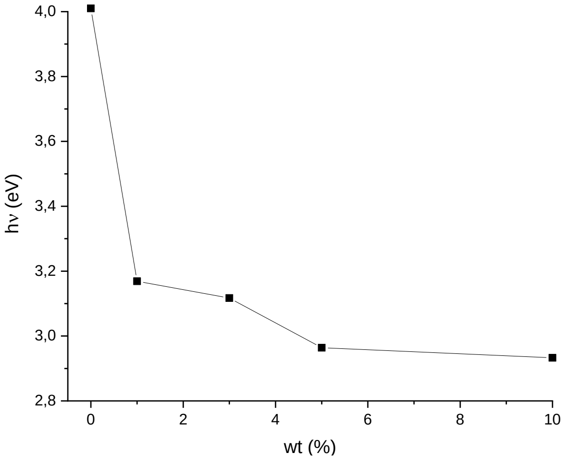


Fig. 8. Dependence of the width of band gap energy E_g on the concentration of fullerene C_{60} in the PS matrix.

Table 2. Values of the optical band gap energy (E_g) for different PS-C_{60} samples, determined from the wavelength of the absorption edge.

Sample	Wavelength of the absorption edge, nm	E_g, eV
PS	358	3.972
PS+1% C_{60}	461	2.092
PS+3% C_{60}	477	2.039
PS+5% C_{60}	481	3.028
PS+10% C_{60}	526	1.854

The decrease in E_g value in PS indicates that the incorporation of C_{60} nanoparticles in PS leads to a weakening of its dielectric properties and acquisition of semiconductor properties by the matrix. This phenomenon may also be related to the formation of defects in the polymer matrix, which can lead to the creation of localized sub-levels in the optical band gap and, as a result, to a decrease in the energy width of the band gap.

4. Conclusion

The work has shown that the incorporation of carbon-containing nanocomposite additives of fullerene C_{60} at different concentrations into the polystyrene matrix leads to changes in the optical properties of the matrix. The main optical parameters of the PS polymer films doped with fullerene C_{60} were determined. The values of the optical energy band gap (E_g) of the prepared PS-C_{60} polymer films demonstrate a tendency to decrease with increasing fullerene concentration.

The obtained research results allow suggesting that fullerene C_{60} nanoaditives, as promising modifying additives improving the physical and mechanical properties of composite materials, when introduced into polymer materials, allow giving them unique properties and making it possible to create new demanded materials. Such materials can be used in the field of improving the operational characteristics of various materials based on them, in solar elements, as well as for the development of components of new electronic devices.

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