JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 25, No. 7-8, July – August 2023, p. 380 - 386

Fabrication and controlling of physical properties of rhodamine 6G-polystyrene film by low doses of gamma-irradiation

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The impact of irradiation by gamma rays with different doses on optical properties of polystyrene/Rhodamine 6G films was examined. FTIR spectrum revealed the absence or no occurrence of the interaction between gamma rays and PS/Rh6G films, which makes them chemically stable. The PS/Rh6G optical properties UV-VIS were assessed in the 200-900 nm wavelength range. Experimental research has demonstrated that increasing the gamma radiation energy improves the PS/Rh6G film's absorbance, absorption coefficient, imaginary and real dielectric constant, refractive index, extinction coefficient, and refractive index. With an increase in irradiation, PS/Rh6G films transmittance and energy band gap diminish.

(Received March 25, 2023; accepted August 10, 2023)

Keywords: Gamma irradiation, Rhodamine 6G dye, PS polymer, Optical properties, FTIR

1. Introduction

Polystyrene (PS) is an amorphous thermoplastic that is hard, stiff, tasteless, easy to fabricate with heat, thermally stable, low specific gravity, and inexpensive. It also has great electrical characteristics for insulating uses. When heated above its glass transition temperature (for molding or extrusion), it flows, but when cooled down, it returns to its solid (glassy) condition. Pure solid polystyrene is an inflexible and colourless material that is rigid. Polystyrene can be transparent or can be made to take on various colours[1–4].

The Rhodamines are typically effective and structurally based on xanthenes in the (500-700 nm) wavelength range. When employed as an effective medium in dye lasers, Rh6G chloride has high efficiency. Rh6G chloride is a red powder with the chemical formula $C_{27}H_{29}ClN_2O_3$, is highly soluble, and has a distinctive molar mass (479.02 g/mole). [5, 6].

Rh6G dye is utilized in a variety of applications, including concentrator-equipped solar cells, optical switching, optical limiting power, optical communications, gain medium, photonics devices, and dye lasers [7–9].

Depending on the filler's chemical behavior and how the filler interacts with the polystyrene (PS), the inclusion of any organic dyes into the PS matrix affects the chemical as well as physical properties regarding PS. Due to its numerous characteristics, including a strong transparency and high melting point, PS, a thermoplastic polymer, is frequently used in the industrial applications. Because of the existence of phenyl rings and ionization, polystyrene is the most stable polymer among all polymers when exposed to ionizing radiation, like electron and gamma rays [10]. Ionizing radiation exposure has changed physical and chemical characteristics of the polymers by a variety of mechanisms, including bond breaking, crosslinking, chain scission, molecule and atomic excitation, and ionization [11]. In addition, such procedures are accountable for introducing imperfections into the polymer matrix. Furthermore, ionizing radiation causes unsaturated carbonyl group in polystyrene, which modifies both its optical and luminescent properties. There are a limited number of research papers on the alteration of the optical characteristics of organic dyes based on polystyrene.

Polymeric materials have drawn substantial attention from researchers in a few commercial and multidisciplinary tasks due to its advantageous characteristics (flexibility, durability, lightness, thermal stability, high strength, resistance to corrosion, etc.). Radiation can effect on polymer structure, molecular weight and consequently on its physical characteristics [12]. As a result, polymer-based radiation (electromagnetic, gamma, etc.) has received a tremendous amount of interest from scientists.

Ghaidaa J. Habi [13], impacts of the gamma radiation on specific optical characteristics of the PMMA polymer film specimens that have been blended with 9% phenolphthalein (phph). The experiment revealed that absorbance as well as extinction coefficients increase proportionately with the exposure time. When the time of the gamma ray exposure on film layer of produced samples has been increased, optical gap energy characteristic for the forbidden as well as allowed electronic transition values dropped.

K. Marzouki et. al. [14], silica xerogels doped sucrose has been made using the sol-gel method, then subjected to various doses of high energy (Co^{60}) gamma radiation at room temperature. Variations in the gap energy are obvious in the wavelength range of UV-visible as well as FTIR spectra regarding irradiated and unirradiated xerogels with varied gamma doses of radiation. It has been discovered that the energy gap related to examined silica xerogels reduced when dosages of gamma radiation were increased.

Mahasin. F. Hadi.Al-Kadhemy et. al. [15], researchers have looked at FTIR transmission spectra regarding PS, coumarin-doped polystyrene films, and coumarin laser dye with a range of coumarin solution doping ratios. Regarding all films, such spectra have been measured and characterized both prior to and following various Alpha exposure durations. Every sample was made using the casting procedure. By generating an IR absorption spectrum when the coumarin solution's doping ratio is increased and when it is exposed to an alpha source of radiation, FTIR can confirm the chemical interactions between polystyrene sheets and coumarin dye molecules. After irradiation, some bonds vanished.

Maxime Royon et. al. [16], in particular, γ-rays have an impact on the observed PL regarding organic-inorganic TiO_2-SiO_2 sol-gel films that have been doped with the R6G, which are photocurable. FTIR spectroscopies are used to evaluate both the chemical alterations as well as the radiation-induced change in the refractive index. The results show that at an accumulated dose of 1 MGy, a photo-induced polymerization associated with consumption of CH=C, Si-OH, and Si-O-CH_3 groups in order to produce Ti-O and Si-O bonds leads in a refractive index drop of $7x10^{-3}$ at 633 nm. All such results show the resistance to strong γ-ray irradiation regarding host matrix (TiO_2-SiO_2) as well as the R6G fluorophores.

The major aim of the presented study is to investigate effects of Gamma irradiation in different low doses (1, 3, 5, 8, and 10) KGY on physical properties of Rh6G dye doped PS film. Physical properties included FTIR spectra and calculate all optical constants.

2. Theoretical part

Equation (1) gives the connection between incident and transmitted light intensity [17]:

$$I = I_o\, e^{-\alpha t} \qquad (1)$$

where (α): is the optical absorption coefficient, (t): is film thickness, and absorbance is defined by A=log (Io/I), where (I) and (Io) represent transmitted light and intensities of incident, respectively.

From optical absorbance spectra, optical absorption coefficient (α) can be calculated by using the following relationship (2) [17]:

$$\alpha t = \log (I_o / I) = 2.303\, A \qquad (2)$$

The extinction coefficient (k) is linked to absorption coefficient (α), as in the equation below [18, 19]:

$$k = \frac{\alpha\lambda}{4\pi} \qquad (3)$$

where λ: represents incident light wavelength.

From the transmission (T) and the absorption (A) spectra, reflection (R) spectrum is estimated based on equation (4) [20]:

$$R + A + T = 1 \qquad (4)$$

The refractive index (n) relies on reflectance (R) and extinction (k) coefficients, as in the equation below [17]:

$$n = [(\frac{1+R}{1-R})^2 - (k^2 + 1)]^{\frac{1}{2}} + \frac{(1+R)}{(1-R)} \qquad (5)$$

The direct and indirect transition of absorption edge may be calculated, as in Tauc equation [21].

$$\alpha h\upsilon = B(h\upsilon - E_g \pm E_p)^x \qquad (6)$$

where Ep: phonons energy, Eg: represents optical energy band gap, B: represents a constant, hυ: represents photon energy and x: is constant, and may take values (2, 3) for allowed and forbidden indirect transition, respectively and (1/2, 3/2) for the allowed and the forbidden direct transitions, respectively.

The capability of the material to polarize has been clarified by dielectric constant, as in the following equation [22]:

$$\varepsilon = \varepsilon_r - \varepsilon_i \qquad (7)$$

The dielectric constant has been divided to two parts, which are imaginary (ε_i) and real (ε_r), as in the following equations [17]:

$$\varepsilon_r = n^2 - k^2 \qquad (8)$$

$$\varepsilon_i = 2nk \qquad (9)$$

3. Experimental work

3.1. Material used

Chemical formula of PS is $-[-CH(C_6H_5)-CH_2]^{-n}$ with molecular weight 23700g/mole. The chemical formula of the Rh6G dye is ($C_{20}H_6N_2O_9Br_2Na_2$) with the molecular weight of 624.06 g/mole. Dichloromethane has the chemical formula of CH_3ClCH_3Cl with molecular weight 84.93 g/mole used as solvent for both dye and polymer.

3.2. Preparation of film

The casting technique applied to prepare Rh6G-PS film. The necessary quantity (0.5g) of polymer was dissolved in Dichloromethane (10 ml) to create PS polymer solution. R6G solution has been added to the PS solution and well mixed at the magnetic stirrer after being thoroughly mixed at the magnetic stirrer. To create a homogeneous Rh6G/PS film, the mixture has been placed into a glass petri dish and allowed to sit for 24 hrs at room temperature. Rh6G has been selected at a concentration of 1×10^{-5} mole /litter.

3.3. Devices used

With the use of the ^{60}Co Gamma Cell-900, samples have been exposed to radiation at several dosages (1, 3, 5, 8, and 10) kGy, at dose rate of 20 Gy/h, producing 1.17 & 1.33 MeV mono-energetic, and at a half-life of 5.30 years. The utilized source was installed in Dept. of Physics, College of Science, Baghdad Univ., Iraq, and constructed into a lead container with chemical inserting facilities without the exposure of operator to the radiation. UV-Vis. spectrophotometer type (T70/T80 Series UV/Vis Spectrometer) was utilized for the purpose of calculating absorbance and transmission spectra in 200-900 nm wavelength range. FTIR spectra regarding as-prepared films were measured using a Bruker ATR spectrophotometer.

4. Results and discussions

The FTIR spectroscopy of PS/Rh6G films for before and after irradiation by gamma ray at different doses (1, 3, 5, 8 and 10) KGy are illustrated in Fig. 1. Five peaks at (3082 - 2849cm^{-1}) range, allocated to stretching vibration regarding C-H bonds in aromatic rings, peaks at (1601, 1583, 1492, 1451) cm^{-1}, because of the stretching vibration regarding C=C bond on the benzene ring, and the peaks at (1028 - 695) cm^{-1}, related to C-H out-of-plane bending vibration of benzene rings, are the major characteristics of PS. It was observed that there was no variation in peaks locations of PS/Rh6G films with change the dose of gamma ray. The transmittance intensities increasing negligible with the rise in gamma ray dose because the PS/Rh6G films contains a number of benzene rings, which leads to the attenuation of the excitation energy caused by gamma rays by resonance inside the benzene rings, this reduces the effect of gamma rays on films. This indicates that PS/Rh6G films is almost chemically stable up to radiation dose 10 KGy [23–29].

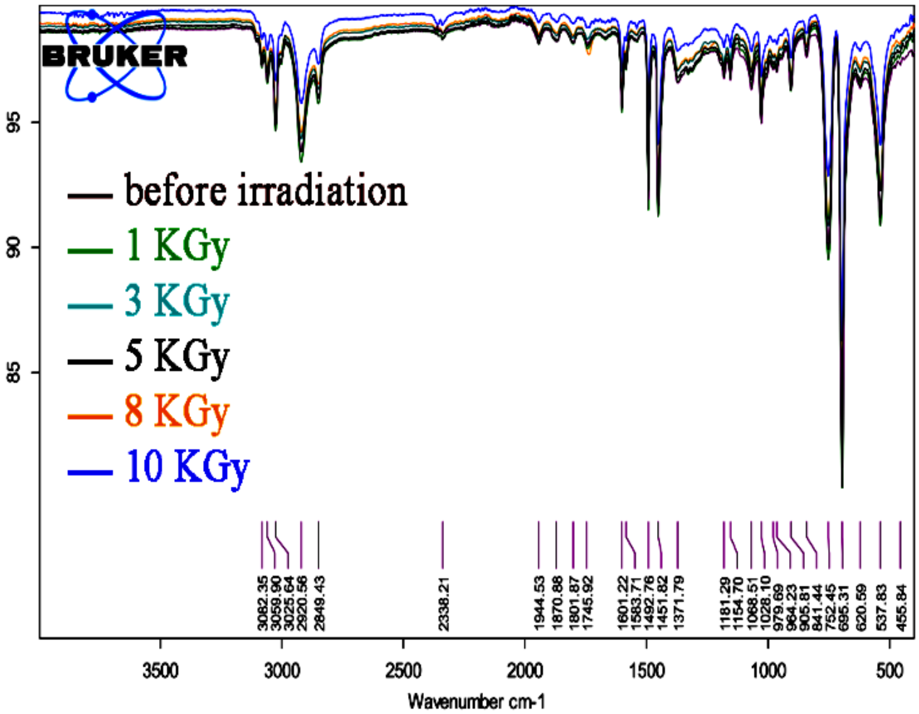

Fig. 1. The FT-IR spectra of PS/Rh6G films at before and after the irradiation with various dosages (1, 3, 5, 8 and 10) KGy of gamma rays (color online)

Fig. 2 shows the impact of gamma rays on absorption spectrum for PS/Rh6G film before and after irradiated by different doses (1, 3, 5, 8, and 10) KGy. The absorption spectrum appears two peaks at (515 and 350) nm and two shoulders at (480 and 545) nm, which represent the spectrum of Rh6G dye that dominates the spectrum of polystyrene polymer that has an absorption peak between (240 - 280) nm [16], [25–27], [30], [31]. The movement or excitation of electrons from low levels (ground state) to higher energy levels that have been characterized by molecular orbital is caused by the absorption of light energy with wavelengths that are between visible and ultraviolet rays by the PS/Rh6G polymeric composites. When gamma rays interact with polymeric composites, new defects and sub-energy levels are created. From the figure it is observed that increasing the radiation dose leads to a raise in intensity of absorption and this is imputed that irradiation leads to an increasing in the number of dipoles, also that is lead to increase of reflectance as illustrated in the Fig. 3. Therefore, the increase in absorption results in decrease in the transmittance with increasing radiation dose, as shown in the Fig. 4 [32–35].

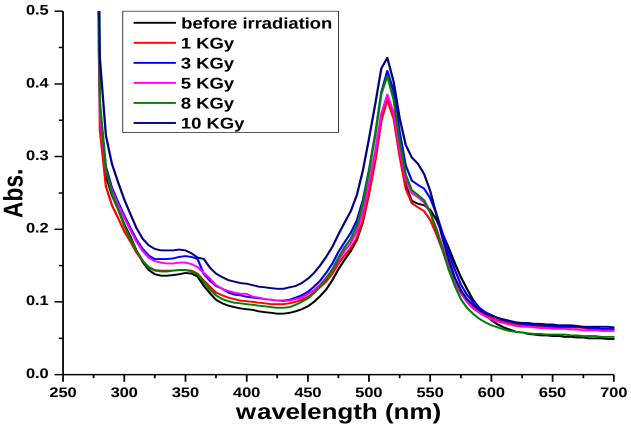

Fig. 2. Absorption spectrum of PS/Rh6G films at before and after irradiation with various doses (1, 3, 5, 8 and 10) KGy of gamma rays (color online)

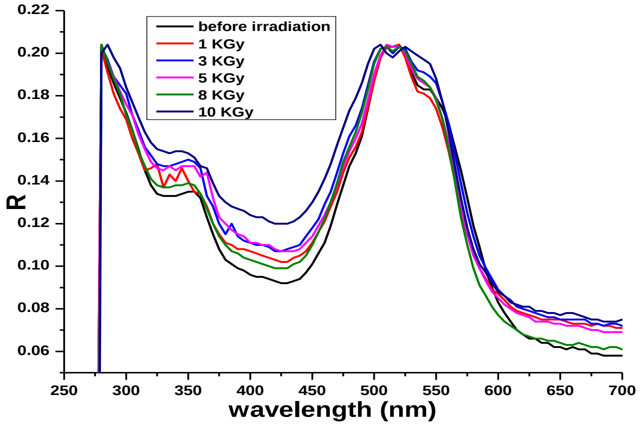

Fig. 3. The reflection spectrum of PS/Rh6G films at before and after irradiation with various doses (1, 3, 5, 8 and 10) KGy of gamma rays (color online)

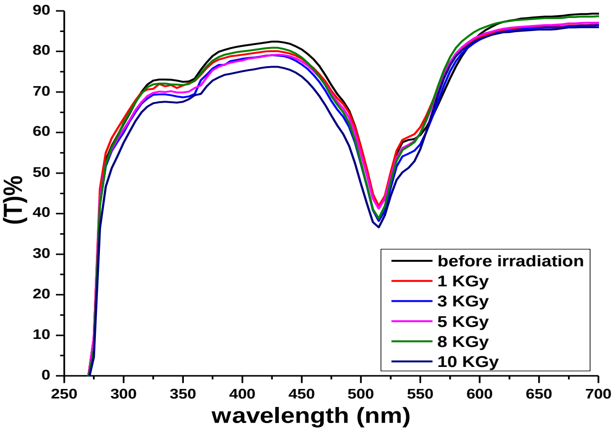

Fig. 4. The transmission spectrum of PS/Rh6G films at before and after irradiation with various doses (1, 3, 5, 8 and 10) KGy of gamma rays (color online)

Equation 2 could be utilized to compute absorption coefficient. As it has been illustrated in Fig. 5, it has been noticed that the data showed an absorption coefficient value less than (10^4 cm^{-1}) indicated that it possesses indirect band gap energy. Equation (6) was used for computing band gap energy, and results have been reported in Table 1. As shown in Fig. 6, it has been observed that optical band gap has been reduced from (2.65) eV prior to irradiation to (2.35) eV as the gamma ray irradiation energy increased. The complex gamma irradiation-related phenomena, like free radical production, polymer chain scission, unsaturation, cross-linking, and/or carbon cluster formation, are to blame for the reduction in optical band gap energy, because of the polymer chain's emission of hydrogen and/or other volatile gases. Those events played a part in the development of structural flaws which increased structural disorder in irradiated films. The density of states model predicts that when the amorphous phase's degree of disorder increases, optical band gap energy will decrease, which results in increasing the polymer's conductivity [36–39].

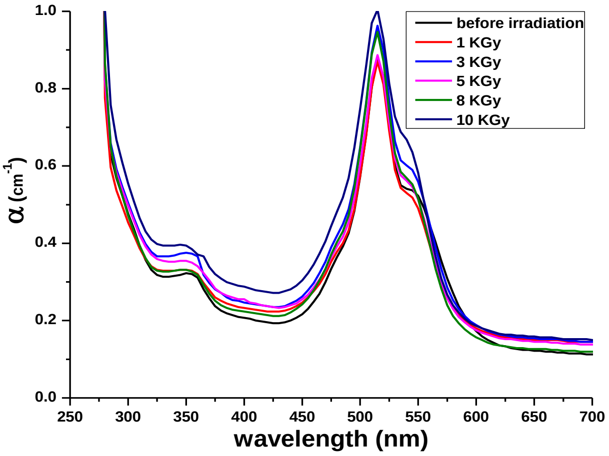

Fig. 5. Absorption coefficient (α) of PS/Rh6G films at before and after irradiation with various doses (1, 3, 5, 8 and 10) KGy of gamma rays (color online)

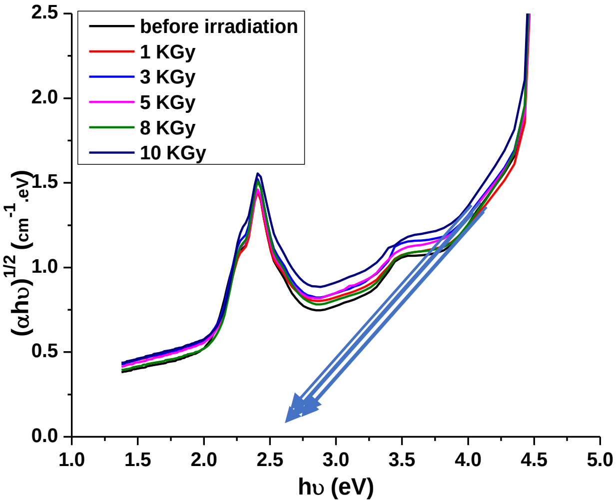

Fig. 6. The indirect energy band gap $(\alpha h\upsilon)^{1/2}$ of PS/Rh6G films at before and after irradiation with various doses (1, 3, 5, 8 and 10) KGy of gamma rays (color online)

Table 1. Energy band gap value of PS/Rh6G films at before and after irradiation with various doses (1, 3, 5, 8 and 10) KGy of gamma rays

Samples	Optical Energy Band Gap E_g (eV)	Phonons Energy E_p (eV)
Before irradiation	2.65	0.19
1 KGy	2.48	0.22
3 KGy	2.43	0.27
5 KGy	2.42	0.31
8 KGy	2.57	0.23
10 KGy	2.35	0.26

Equations 3 and 5 have been used to determine the extinction coefficient as well as refractive index, respectively. For PS/Rh6G films prior to and following exposure to different doses of gamma radiation (1, 3, 5, 8 and 10) KGy. Because of its dependence on reflectivity, the refractive index rises as the irradiation dose rises, as seen in Fig. 7. As can be seen in Fig. 8, the extinction coefficient (k) rises as the irradiation dose rises because it depends on absorption, which is impacted by the rise in irradiation dose [40], [41].

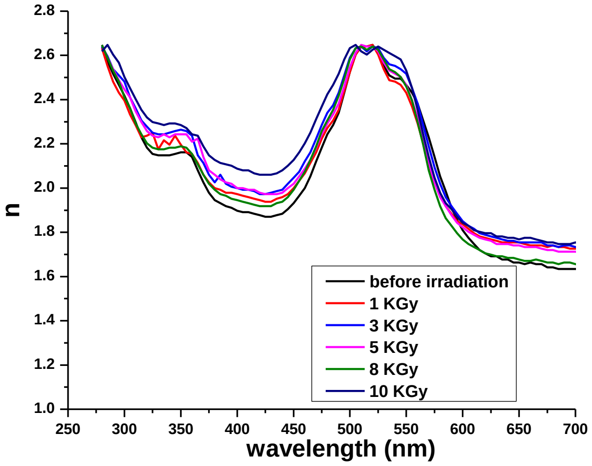

Fig. 7. The refractive index of PS/Rh6G films at before and after irradiation with various doses (1, 3, 5, 8 and 10) KGy of gamma rays (color online)

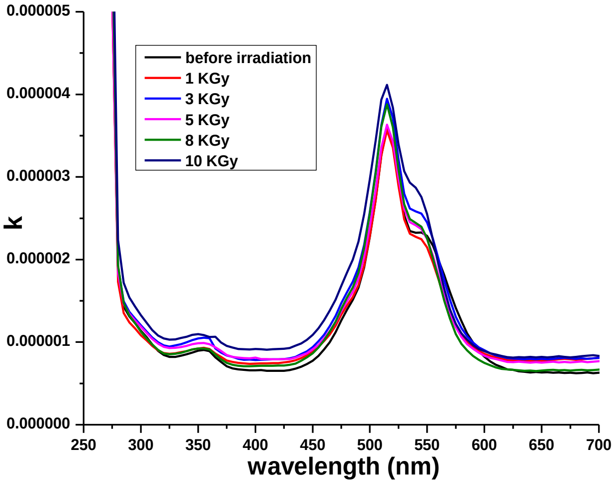

Fig. 8. The extinction coefficient of PS/Rh6G films at before and after irradiation with various doses (1, 3, 5, 8 and 10) KGy of gamma rays (color online)

Equations 8 and 9 could be used for calculating the real and imaginary dielectric constants for PS/Rh6G films, respectively. Figs. 9 and 10 depict the relationship between the imaginary and real dielectric constants of PS/Rh6G films as a function of light wavelength both prior to and following exposure to different doses of gamma radiation (1, 3, 5, 8 and 10) KGy. We might draw the conclusion that as the radiation dose increases, real and imaginary dielectric constant parts rise as well. This is because the optical constants, like the extinction coefficient and refractive index, have increased as a result of the increase in absorption caused by structural deformations regarding the polymeric films [41–42].

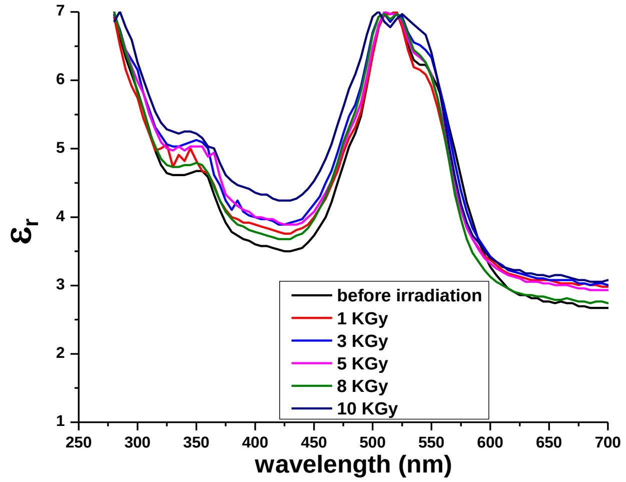

Fig. 9. The real part of dielectric constant for PS/Rh6G films at before and after irradiation with various doses (1, 3, 5, 8 and 10) KGy of gamma rays (color online)

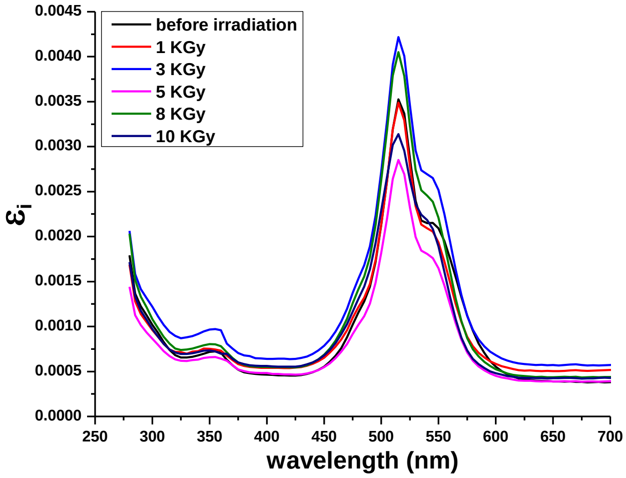

Fig. 10. The imaginary part of the dielectric constant for PS/Rh6G films at before and after irradiation with various doses (1, 3, 5, 8 and 10) KGy of gamma rays (color online)

5. Conclusions

PS/Rh6G films were irradiated with different doses (1, 3, 5, 8 and 10) KGy of gamma rays. From the study FTIR spectrum before and after irradiation, it was observed that there was no effect of gamma rays on PS/Rh6G films, making it chemically stable within these irradiation doses. With an increase in gamma radiation energy, PS/Rh6G films' absorption coefficient, absorbance, extinction coefficient, refractive index, imaginary and real dielectric constant, and other properties change. With the increase of gamma ray intensity, the transmittance and energy band gap decrease.

Acknowledgements

The authors would like to thank Mustansiriyah University (www.uomustansiriyah.edu.iq) Baghdad-Iraq for its support in the present work

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