Global Journal of Scientific Researches
Available online at gjsr.blue-ap.org
©2020 GJSR Journal. Vol. 8(2), pp. 23-31, 05 Jul

Effect of Gamma Irradiation on The Optical Properties of PVA / Ag Nano-composite

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Received: 05 June, 2020 *Accepted: 16 June, 2020* *Published: 05 July, 2020*

ABSTRACT

The main focus of the present work to investigated the effect of the gamma irradiation on the optical properties and energy band gap of the Nano composite polyvinyl alcohol (PVA) doped with silver nanoparticles (Ag) thin films were prepared using the signification and casting techniques.
The Gamma irradiation emitted from 60Co source with irradiation dose (1, 3, 5, 8, 10 and 15) kGy.
Absorption and transmission spectra have recorded in order to determine the type of electronic transitions and find the value of the optical energy gap. The results indicated that indirect transition expected and the value of energy gap decreased from (4.7 eV) for unirradiated nanocomposite (PVA/Ag) film, after irradiation energy gap is decrease with the increasing doses irradiation.
The radiation effect on the linear coefficient of absorption (α), refractive index (n), coefficient of extinction (k), real and imaginary dielectric constants for all samples were studied.

Keywords: *Nanocomposite, optical properties, gamma irradiation, PVA/Ag nanoparticle*

INTRODUCTION

The advancement of nanoscience in polymeric substances that contain at least one-dimensional nanoscale has considerable interest in advanced materials science research. Nanocomposite polymer is of great importance among classes of nanocomposite materials and has been widely used in a wide range of fields, with special emphasis on medical and biological applications. The physical and engineering properties of the polymer matrix are improved by the addition of nano fillers due to the high volume ratio of the surface area [1].
Poly (vinyl alcohol) (PVA) is one of the most important polymers available in the form of powders, fibers and film. This is a well-known water soluble polymer, commonly used as warp sizing agents and paper coating agents, adhesives, and films. PVA has recently been the subject of Intensive research because it has many industrial applications and relatively low manufacturing costs [2].
The effect of radiation on polymeric materials is of great importance as it enables the physical properties of polymers to be modified and improved. Irradiation of polymeric materials with gamma rays, x-rays, accelerated electrons and ion beams, for example, leads to the formation of reactive intermediates and free radicals, which then lead to significant reactions such as degradation or cross-linking. Those interactions were regulated by the dose of radiation provided [3].
Different polymers have different reactions affected by the dose of radiation, which are inherently related to the chemical structure of the polymers. Hence, polymer properties such as the optical, electrical, mechanical, and chemical properties are modified [4].

M. F. H. Al-Kadhemy et al [5], gamma ray effect on PMMA / PS blends at different concentrations has been worked out. Optical constants such as absorption coefficient, refractive index are calculated and the optical energy gap (direct/indirect) was studied before and after irradiation. Transmittance, absorbance and reflectance spectra of pure and blend polymers are investigated.

A.J.Almusawe et al [6], studies the effect of gamma irradiation on the optical properties of bromocresol green dye doped with polymethylmethacrylate thin film and shows increased optical properties with increased radiation dose but decreased optical energy gap.

H.S. Rasheed et al [7], studied the effects of ionizing radiation on the properties of the nanocomposites composed of Poly (vinyl alcohol) (PVA), Poly (acrylic acid) PAA have been prepared with different concentrations of aluminum (III) oxide (Al_2O_3) nanoparticles and thicknesses by using the casting method. These films were irradiated with (50kGy) of ^{60}Co gamma rays. The results show that the effect of γ-irradiation leads to increase the absorbance, extinction coefficient (k),the index of refraction(n) and the dielectric constants(ε_r and ε_i) of the real and imaginary while the energy gap (Eg) and the transmittance decreases.

Z. I. Ali et al [8], studied optical and structural properties of PVA / Ag with gamma ray effect, show that the absorption peak increases with increased irradiation dose and concentration of $AgNO_3$, while the optical band gap decreases with an increase in molar concentration of $AgNO_3$ from 0.005 M to 0.1 M for all irradiated samples. The XRD pure PVA pattern exhibits a strong and wide diffraction peak located at 2θ = 19.66°, which is due to the crystallinity part, where the irradiated Ag / PVA nanocomposite samples show four new diffraction peaks at 2θ = 37.8 °, 43.96 °, 64.34 ° and 77.48°, which show that the Ag nanoparticles are formed in the PVA matrix.

The aim of the present work is to prepare (PVA / Ag) nanocomposite using the casting method. The nanocomposites of PVA / Ag thin film will be irradiated by γ -rays and then the optical properties will be tested before and after irradiation.

2. Theoretical Part

The relationship between the intensity of incident and transmitted light is given by the equation (1) [9]

$$I = Io\ e^{-\alpha t} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where (Io) and (I) are the intensities of the incident and transmitted light,
respectively, (α) is the optical absorption coefficient; (t) is the thickness of film and absorbance is defined by A=log (Io/I).
The optical absorption coefficient (α) can be calculated from the optical
absorbance spectra by using the relation (2) [9]:

$$\alpha t = \log\left(\frac{I_o}{I}\right) = 2.303A \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The extinction coefficient (K) is related to absorption coefficient (α), by the following equation [10]:

$$K = \frac{\alpha\lambda}{4\pi} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where, λ is the wavelength of incident light.
The reflectance (R) can be calculated from the values of the absorbance and transmission coefficient from the equation:

$$R = 1 - (A + T) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

The refractive index (n) depends on the reflectance (R) and extinction
coefficient (K) and it can be calculated from the following equation[11]:

$$n = \sqrt{\frac{4R}{(R-1)^2} - K^2} - \frac{(R+1)}{(R-1)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

The absorption edge for direct and indirect transition can be obtained in the view of the proposed by Tauc et al. [12]

$$\alpha h\upsilon = A(h\upsilon - E\,g)^r \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Where (h υ) is the energy of photon, (A) is the proportional constant,
(Eg) is the allowed or forbidden energy gap of direct and indirect transition and (r) is constant depended on the electronic transition, r=1/2, 3/2, 2 or 3 for allow direct, forbidden direct, allow indirect and forbidden indirect transition, respectively.
The Dielectric constant clarified the ability of material to polarization
and can be express by the following equation:

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

The dielectric constant is divided into two parts real (ε_r) and imaginary (ε_i) and described by the following equations:

$$\varepsilon_r = n^2 - K^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

$$\varepsilon_i = 2nK \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

3. Experimental Work

Poly (vinyl alcohol) used in this research as host material for silver nano particles because PVA has excellent film forming with the molecular weight M_w=14000 g / mol, melting point 230 ° C [13].

The cast technique was used to prepare films of pure PVA and PVA with Ag nano- particles by dissolving 0.5 gm from PVA with 0.004 gm from silver nanoparticle in 15 ml of distilled water. Stirred for 2 to 3 hours at room temperature by magnetic stirrer (hot plate) in (25 - 35° C) to ensure for fully dissolving. Forming the PVA /Ag films by pouring out the solution in glass plates with diameter (3 cm) and allowed it to evaporate slowly at room temperature for (3 to 4 days) to get homogeneous films. The thickness of pure PVA and Ag / PVA films that found (61.6 and 66) µm, respectively.

The samples were irradiated with irradiation dose(1, 3, 5, 8, 10 and 15) kGy, using ^{60} Co Gamma Cell-900, of strength rate 3.7Ci and dose rate 53 Gy/h, which emits mono-energetic 1.17 and 1.33 MeV, and a half-life of 5.3 years. The source used has been built into a lead container with facilities for interesting chemicals without exposing the operator to the radiation, installed at the physics department, university of Baghdad.

The absorption and transmission spectra were measured by UV-Visible spectrophotometer type (T70/T80 Series UV/Vis Spectrometer) in the wavelength range (200-900) nm.

4. Result and Discussions

4.1 Absorption Spectrum for pure PVA and PVA/Ag Nanocomposite

The absorption spectrum of PVA polymer films and PVA/Ag nanocomposite displayed in figure (1) with maximum peaks at 280 nm with intensities 0.198 and 0.552 for PVA and PVA/Ag nanocomposite respectively, because of Ag nanoparticles could be implanted in the PVA matrix by forming new bonds between them and PVA chains that leads to a drop in the degree of crystallinity. These results matched with the results obtained from A. AbouElfadl [14].

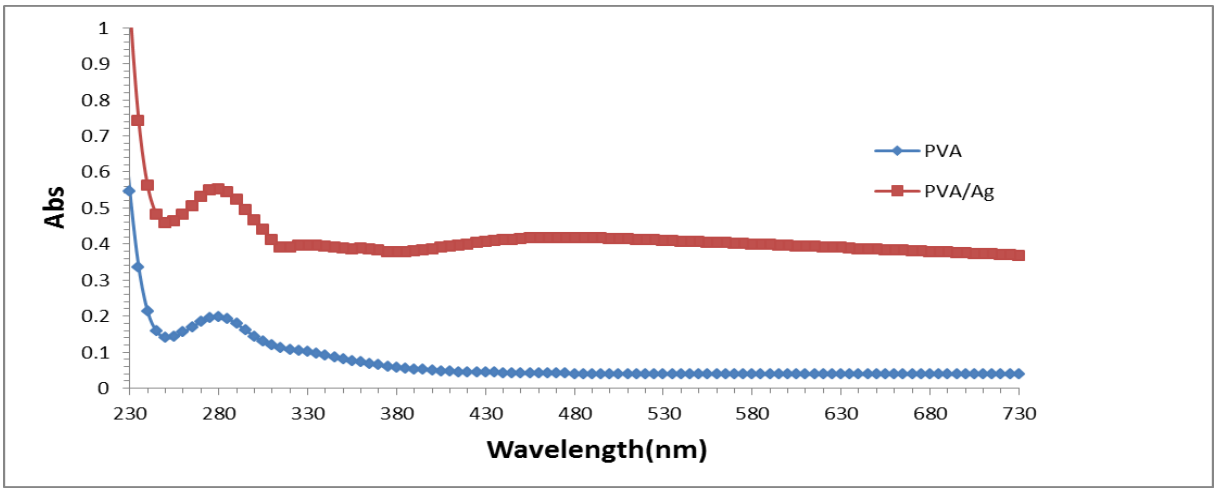

Figure (1) Absorption spectrum of pure PVA and PVA/Ag nanocomposite films before irradiation

The UV/Visible spectra of all samples were acquired by UV-Visible spectrophotometer before and after different gamma irradiation. The results from figure (2) shows the increasing in irradiation dose lead to an increase in the intensities of peaks and there is no shift in the peaks of the spectra, but shows a reduction in the absorbance at (8 and 15) kGy may understood the chains of polymer acquired mobility along with period of experiment scale, afterwards the polymer chains is relax, stress is released. This causes silver nanoparticle to move again, allowing crystals to aggregate which in turn reduces the absorbance and increase wave length. These results are in good agreement with M.G. Pushpanjali, et al [15]. Table (1) shows the highest peak of the absorption spectrum at using doses.

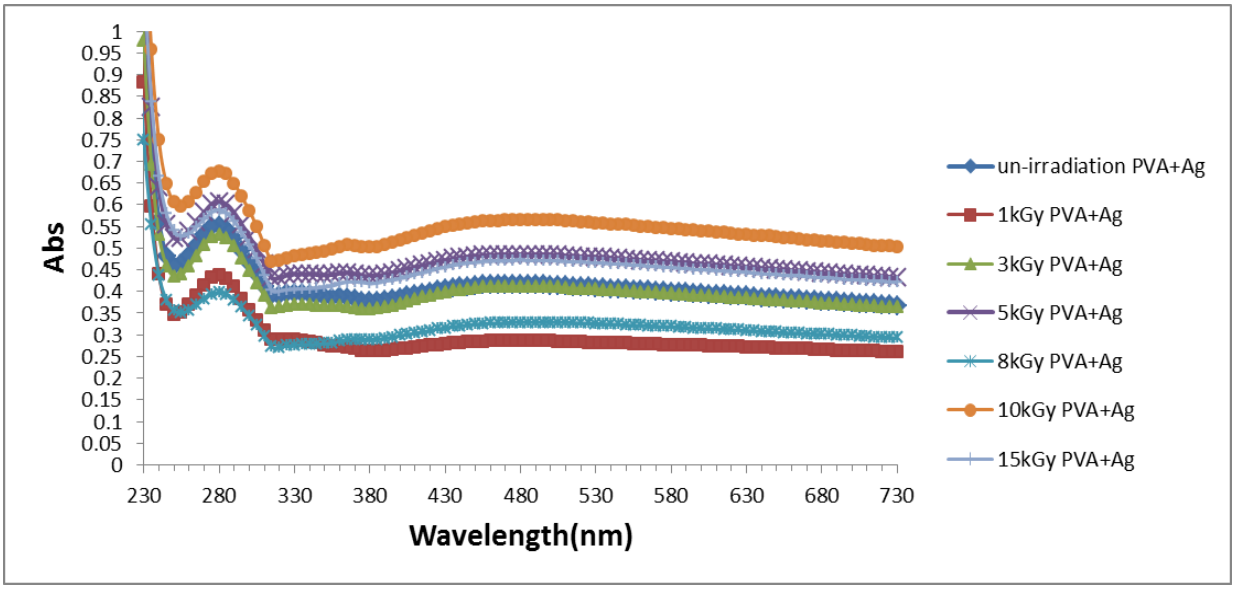

Figure (2) Absorption spectrum of PVA/Ag nanocomposite films, before and after Gamma irradiated to different doses

Table (1) shows the highest peak of the absorption spectrum of PVA/Ag nanocomposite films, Gamma irradiated to different doses

Wavelength(nm)	280	280	280	280	280	280	280
Dose (kGy)	0	1	3	5	8	10	15
Abs.	0.552	0.436	0.532	0.606	0.398	0.677	0.588

4.2 Transmission Spectrum

The transmission (T), defined as the ratio the intensity of transmitted radiation and the intensity of incident radiation that showed in figure (3) of PVA/Ag nanocomposite films, before and after gamma irradiation. The behavior of this spectrum was inverse absorption spectrum.

Figure (3) shows the increase in irradiation dose caused decrease in the transmittance spectra .This is because of the Ag nano-particles absorb and scatter the energy from PVA films. This result is in agreement with M. Vishwas, et al [16].

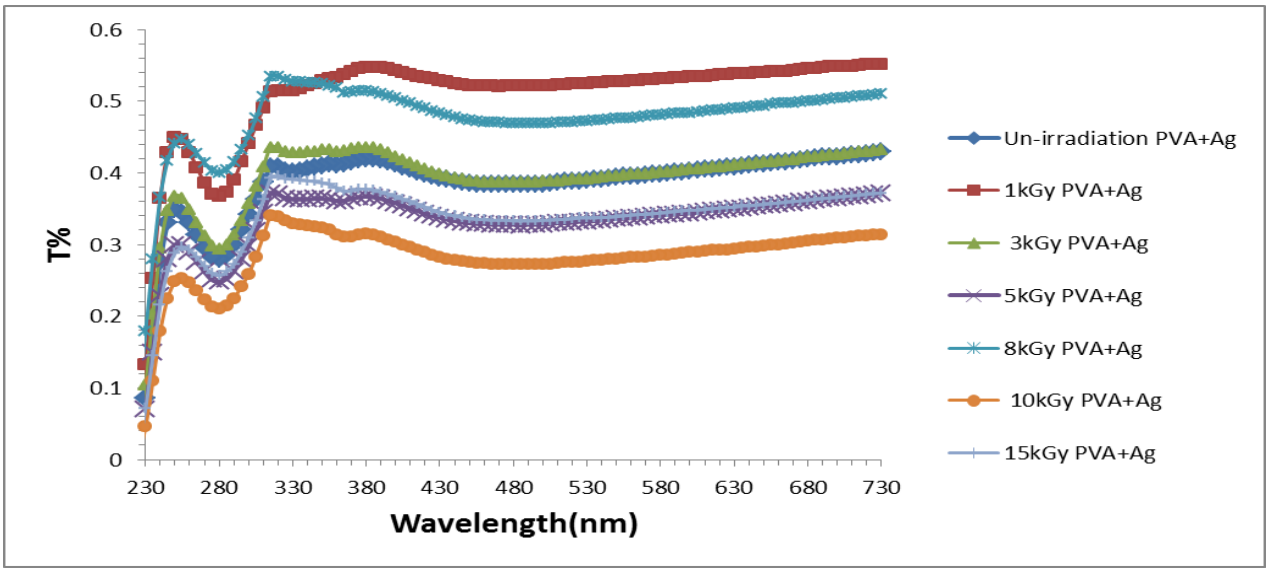

Figure (3) Transmission spectrum for PVA/Ag nanocomposite films, before and after Gamma irradiated to different doses

4.3 Reflection Spectrum

The reflectance can be obtained by using equation(4), this parameter illustrated in figure (4) for PVA/Ag nanocomposite films, before and after gamma irradiation. The maximum reflection of PVA/Ag nanocomposite is 0.202 at wavelength 280 nm for irradiation dose 8kGy as shown in Figure (4) , but the minimum reflection is 0.113 at wavelength 280 nm for radiation dose 10kGy ,this change is due to the degradation processes in the polymer chains[17].

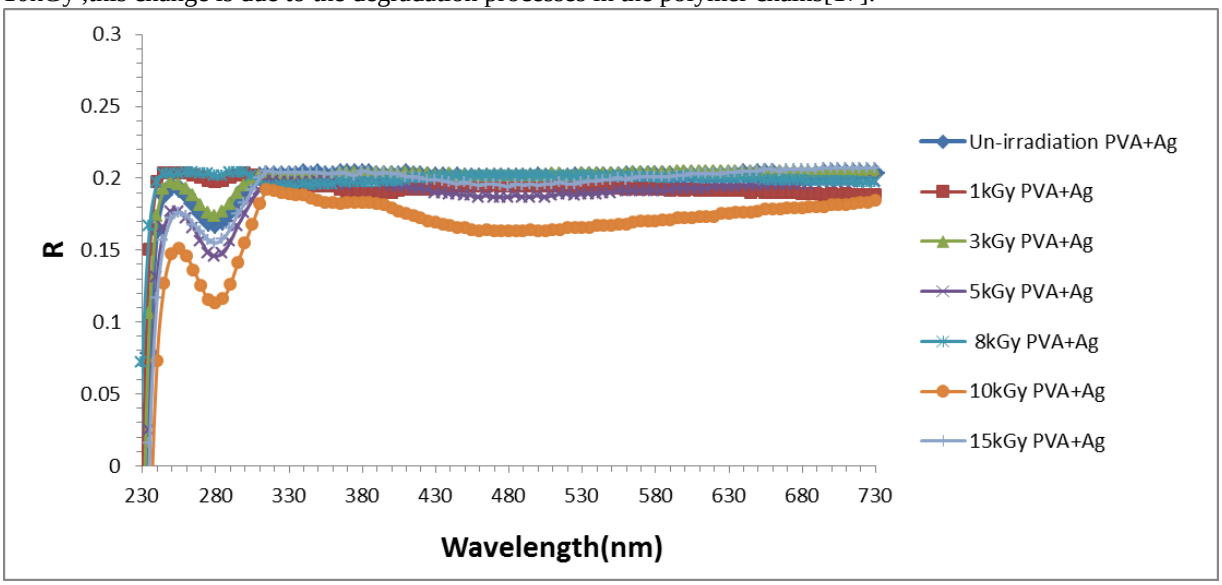

Figure (4) Reflection spectrum for PVA/Ag nanocomposite films, before and after Gamma irradiated to different doses

4.4 Absorption Coefficient

The absorption coefficient (α) is defined as the ability of material to absorption light with a limitted wavelength per unit length and it is a characteristic property for every absorber molecule or ion. From equation (2) the absorption coefficient can be calculate. The value of the absorption coefficient give us information about the nature of electronic transition. When the high absorotion coefficient values ($\alpha > 10^4$ cm^{-1}) at higher energies, the direct electronic transitions expected and the energy momentum preserve of the electron and photon. While the value of absorption coefficient low ($\alpha < 10^4$ cm^{-1})at low energies, indirect electronic transitions expected. Figure (5) showed the absorption coefficient as a function of the wavelength for PVA/Ag nanocomposite films, before and after gamma irradiation.

According to figure (5), the value of absorption coefficient for all samples less than (10^4 cm^{-1}), so that the indirect electronic transitions have been deduced.

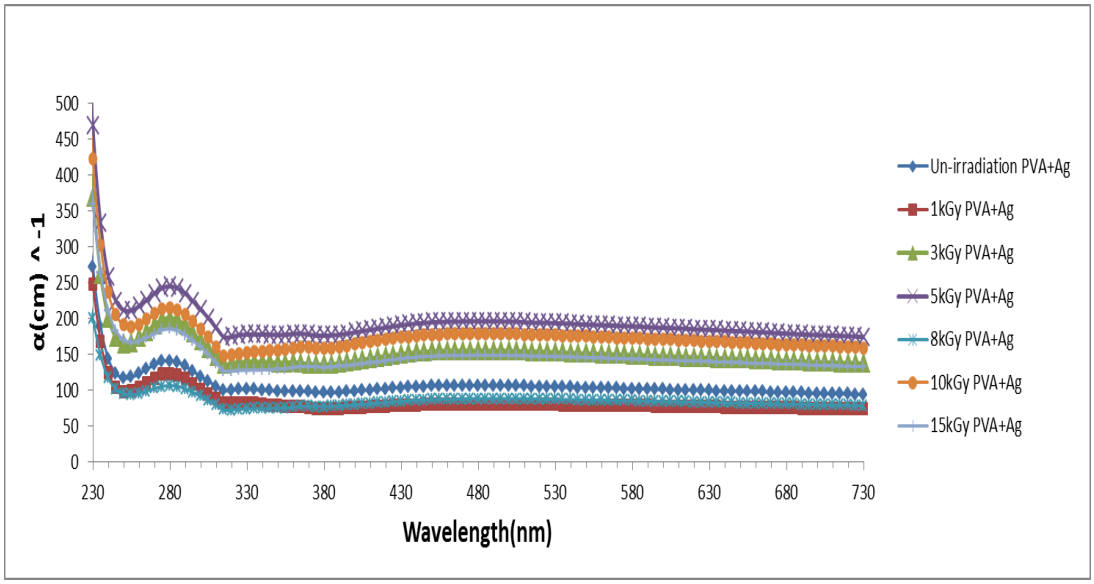

Figure (5) Absorption coefficient for PVA/Ag nanocomposite films, before and after Gamma irradiated to different doses

4.5 Optical Energy Gap

Figure (6) show the relation between absorption edge $(\alpha h\upsilon)^{1/2}$ versus photon energy for PVA/Ag nanocomposite films, before and after gamma irradiation which represent the indirect transition.

Table (2) review the values of energy gap for all samples of PVA/Ag nanocomposite films at different irradiation doses, it can be seen that the values of energy gap decrease with increase irradiation doses, this decrease because of formation of new level in the band gap , which will promote the transfer of electrons from the valence band to conduction band this result is in agreement with Hussein T. Sallom et al[18].

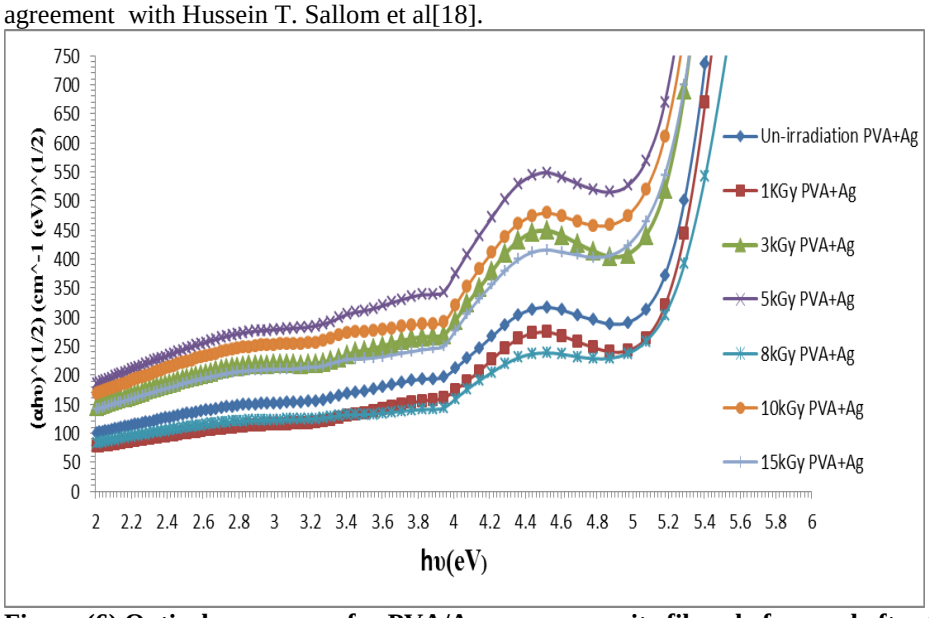

Figure (6) Optical energy gap for PVA/Ag nanocomposite films, before and after Gamma irradiated to different doses

Table (2) Energy gap (E_g) for PVA/Ag nanocomposite films, before and after Gamma irradiated to different doses

Dose (kGy)	0	1	3	5	8	10	15
Energy gap (eV)	4.7	4.68	4.42	4.34	4.28	4.24	4.1

4.6 Refractive Index

The refractive index (n) is a major optical parameter that can be calculated from equation (5) that depend on reflectance, so that the refractive index for all samples is similar to the behavior of reflectance. Figure (7) depicts the behavior of refractive index as a function of the wavelength (λ) for PVA/Ag nanocomposite films at different irradiation doses. This change in refractive index can be due to existing discoveries [17].

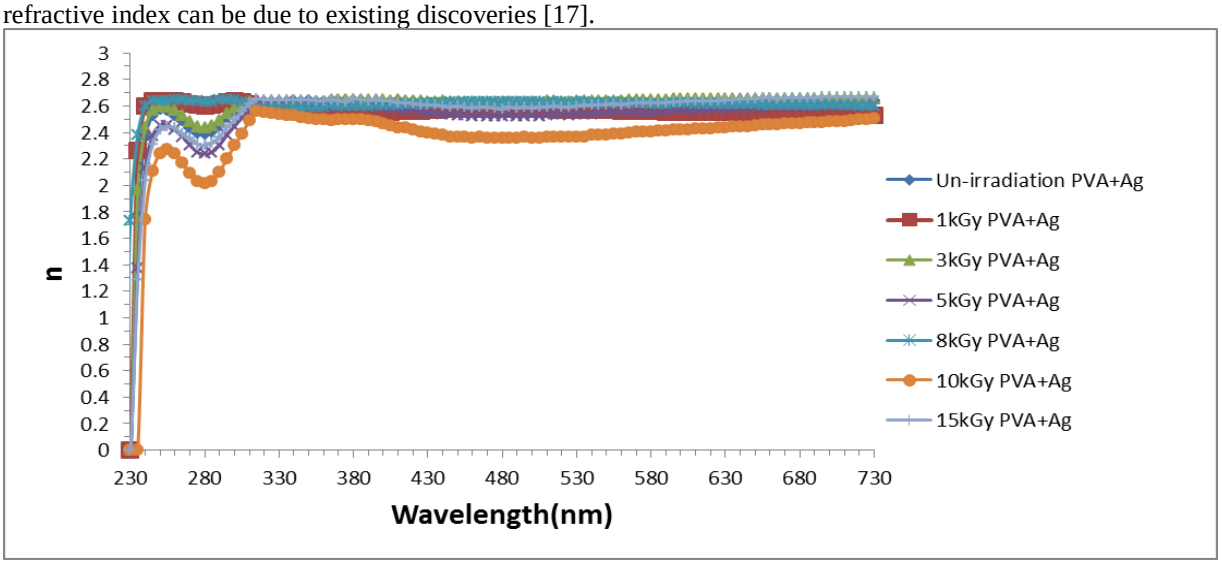

Figure (7) Refractive index for PVA/Ag nanocomposite films, before and after Gamma irradiated to different doses

4.7 Extinction Coefficient

The coefficient of extinction can be calculated by equation (3). The extinction coefficient depends on absorbance, so that the action of all curves is identical to absorption spectrum. Figure (8) illustrates the extinction coefficient for irradiated PVA/Ag nanocomposite films in different irradiation doses.

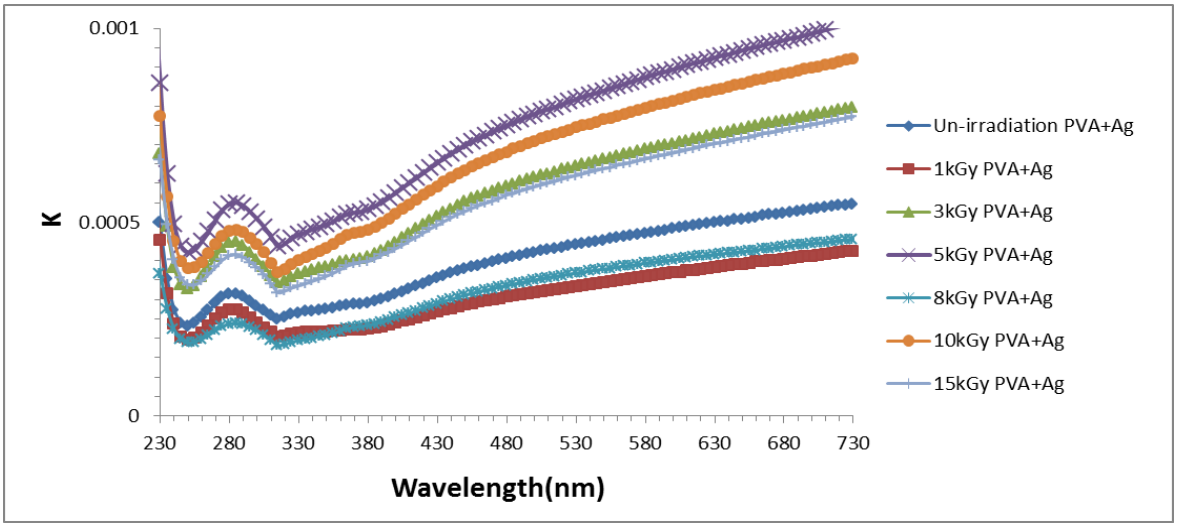

Figure (8) Extinction Coefficient for PVA/Ag nanocomposite films, before and after Gamma irradiated to different doses

4.8 Dielectric Constants

Optical constants are very useful to the quantitative determination of the electronic band structure of solids from information of optical reflectivity, transmission and refraction provide the way to determining the dielectric constants of solid, which is related to the band structure. The real and imaginary parts of dielectric constants were detemined from equation (8) and equation (9), respectively. Figure (9) illstration the real part of dielectric constant for PVA/Ag nanocomposite films in different irradiation doses, the spectrum of the real dielectric constant depends on the square of refractive index, so that the behavior of thise figure is identical to refractive index.

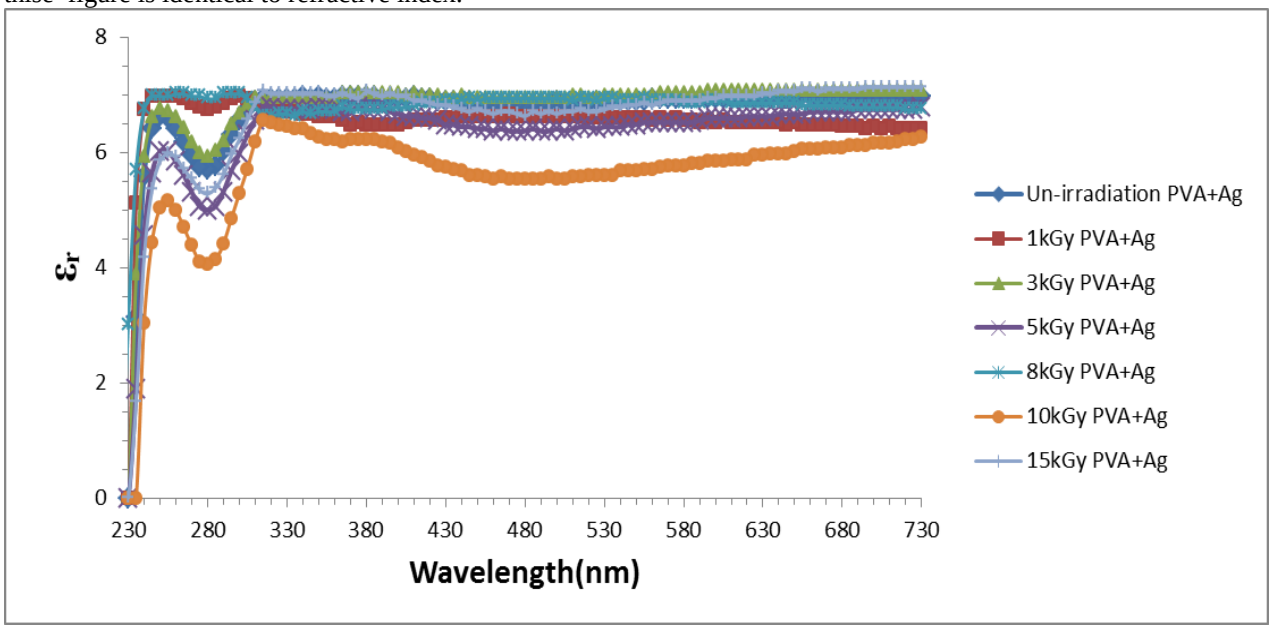

Figure (9) Real dielectric constant for PVA/Ag nanocomposite films, before and after Gamma irradiated to different doses

The imaginary part of dielectric constant for PVA/Ag nanocomposite films in different irradiation is similar to behavior of extinction coefficient. Figure (10) illustrates the imaginary dielectric constant for all samples after gamma irradiation.

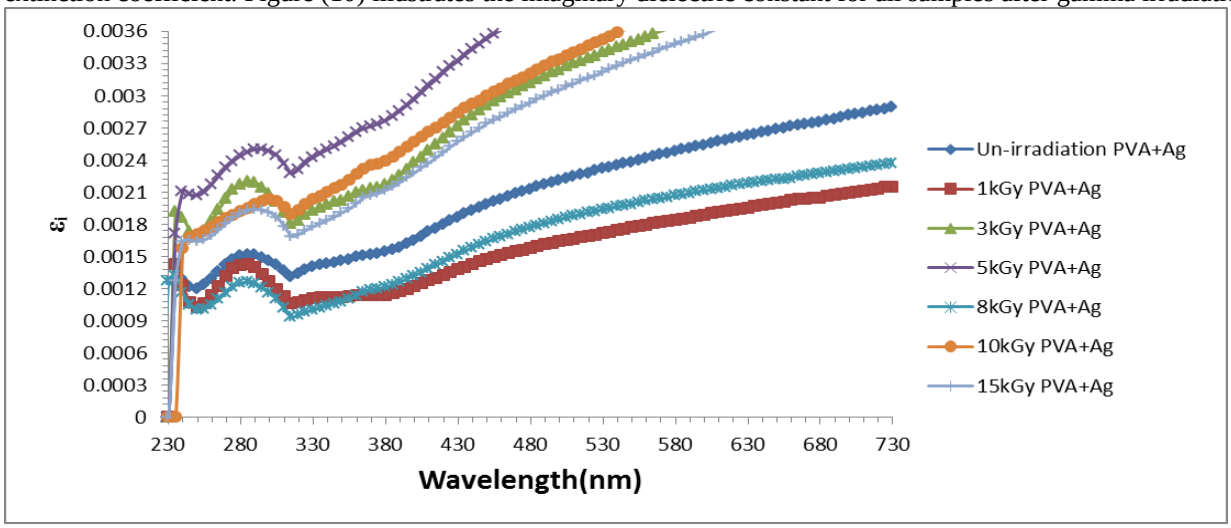

Figure (10) Imaginary dielectric constant for PVA/Ag nanocomposite films, before and after Gamma irradiated to different doses

5. Conclusions

UV/VIS spectrophotometric studies the optical properties for irradiated PVA/Ag nanocomposite films at different irradiation doses , gamma ray lead to degradation in the polymer chains , and indirect bandgap decrease after irradiation , and the value of all optical constant was changing after irradiation .

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

Conflict of Interest
All authors have declared no conflict of interest.

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