

Study of Gamma irradiation effect on the Optical Properties of Bromocresol Green Dye Doped Poly Methyl Methacrylate Thin Films

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Abstract: *In this paper, we investigated the effect of the gamma irradiation on the optical properties and energy band gap of PMMA doped by BCG dye thin films. Films of Poly Methyl Methacrylate doped by 20% BCG doping ratio to prepared concentrations 1×10^{-3} M were deposited on glass substrate using free casting method at room temperature. The optical properties of the films were determined using UV-Visible absorbance and transmittance spectra at the 300 - 800 nm wavelength range. The linear absorption coefficient, the extinction coefficient, and the optical and electrical conductivity were calculated in addition to the energy band gap. The results showed that the optical properties were increasing by increasing the dose irradiation, while the optical energy gap was decreasing with the increasing dose irradiation.*

Keywords: *Thin films, Optical properties, Gamma ray.*

INTRODUCTION

Organic dye doped polymers have a great deal of concern in recent years due to their chain arrangement, behave differently from other familiar materials and hold unique properties due to which they are widely used in various scientific and technological applications[1–3].

The unique properties of polymers such as low density, ability to form intricate shapes, good mechanical strength versatile, electrical properties and low manufacturing cost made them promising materials that have been successfully used as host matrices for dyes. The wide range of polymer applications can be even more extensive by incorporation of filler into polymer matrix, because dispersed filler may increase the concentration of absorptive or fluorescence centers as well as the opto-chemical and opto-physical stability of host polymer[4–6]. Many previous study led to more understanding the relation between polymer structure and physical properties and advantage behavior, thus the optical,

mechanical properties gives complete idea on polymer science [2]. The result of radiation on polymeric materials is of unlimited importance as it allows modifying and improving the physical properties of polymers. The exposure of polymeric materials using gamma rays, X-rays, faster 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. These interactions have been controlled by the given amount of radiation dose [7]. In our study, we report our result on the effect of gamma irradiation on optical constants of doped PMMA films with (BCG) dye.

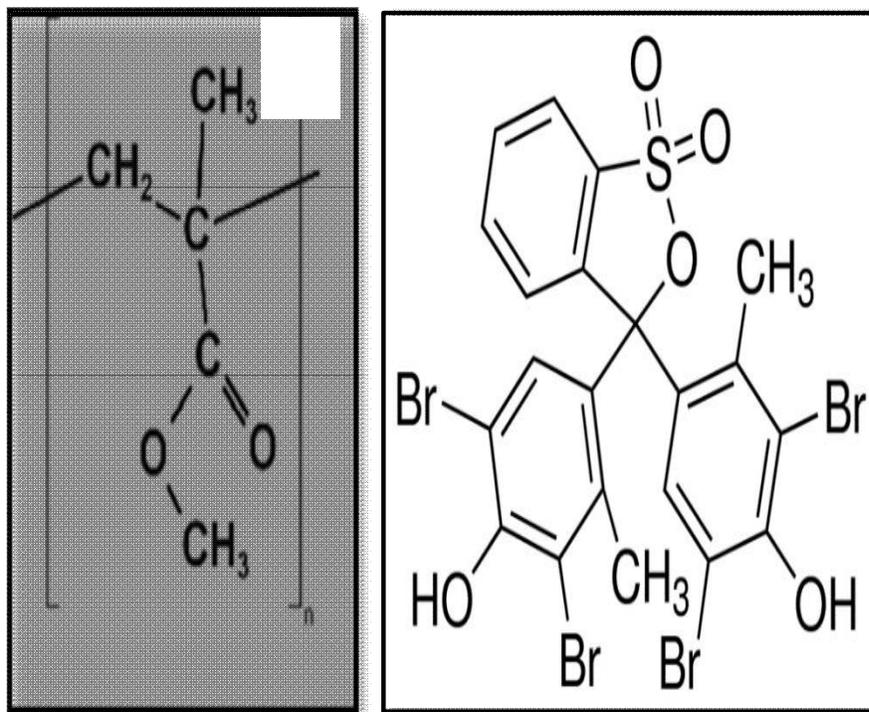
The measurement taken to the optical properties such as absorption coefficient, refractive index and optical energy band gap of dye-doped polymers were investigated using spectroscopic absorbance combined with transmittance measurements of samples before and after irradiation.

Samples Preparation and Irradiation Procedure

The Bromocresolgreen dye from (Sigma-Aldrich), its chemical structure is shown in Figure (1). The bromo group can improve the transparency and the thermal stability of compounds [8, 9].

Polymethyl methacrylate (PMMA) polymer from (Sigma-Aldrich), its chemical structure is shown in Figure (1). It is used as host material for dye due to its excellent optical properties. It is highly amorphous with average M_w of about 120,000, and glass transition temperature 105°C [5]. It is an aromatic polymer made from the aromatic monomer styrene, a liquid hydrocarbon that is commercially manufactured from petroleum by the chemical industry. PMMA is a thermoplastic substance and one of the most widely used kinds of plastic [8-9].

PMMA-BCG films were prepared by casting method. The PMMA solution was prepared by adding 1 g of PMMA powder in 10 ml of chloroform under vigorous stirring for 60 min at 50°C . Each of dye and polymer was dissolved separately in $1 \times 10^{-3}\text{M}$ chloroform. Then, the solution of polymer was mixed with 20% dye solution. Dye-polymer mixture solution with $1 \times 10^{-3}\text{M}$ was casted on a clean glass plate washed in acetone, X and distilled water respectively. Finally, the films were dried in oven at 50°C for 1 hour to remove the residual solvent. The uniform surface films with thickness around $50\text{-}60\ \mu\text{m}$ were obtained [10]. The transmission and absorption of the prepared films were investigated by UV-Vis spectrophotometer in the range (300-800) nm. Then, PMMA-BCG samples with 1 mM concentration, with size $1 \times 1.4\text{ cm}$ were cut from the commercially available sheet. These samples subjected to irradiation using CS137 source with dose rate 0.813 rad/ha and source strength was 7 mCi. The irradiation process divided into two periods 1 hour and 1 week thus the samples were having irradiation in dose range of (0.813-136) rad/h.



(a) (b)

Figure (1):Chemicalstructure and molecularformulaof (a)PMMAand (b)BCGdye.

Results and Discussion

Optical Constant

The figures (2),(3)and (4) shows theAbsorption(A),Transmittance (T)andReflection (R)spectraof PMMA-BCGfilm measuredbyUV-visspectrophotometer beforeandafterirradiation.The results from Figure(2)showstheabsorbancespectraasa functionofthe wavelengthoftheincidentlightforPMMA-BCGfilm.Asitisclear,increasingtheirradiationdoseleadstoanincreaseinthepeakintensity.TheFigure (3) shows the increasein irradiation dose caused decrease intransmittance spectra because the transmissionrelationship withabsorptionisalogarithmic relationship.Inaddition,figure(4)showsthe Reflection spectra (R) for PMMA-BCG films before and after Irradiation where the reflectance R obtainedfromthe relation(1)[11].

$$A + T + R = 1 \quad \dots\dots\dots(1).$$

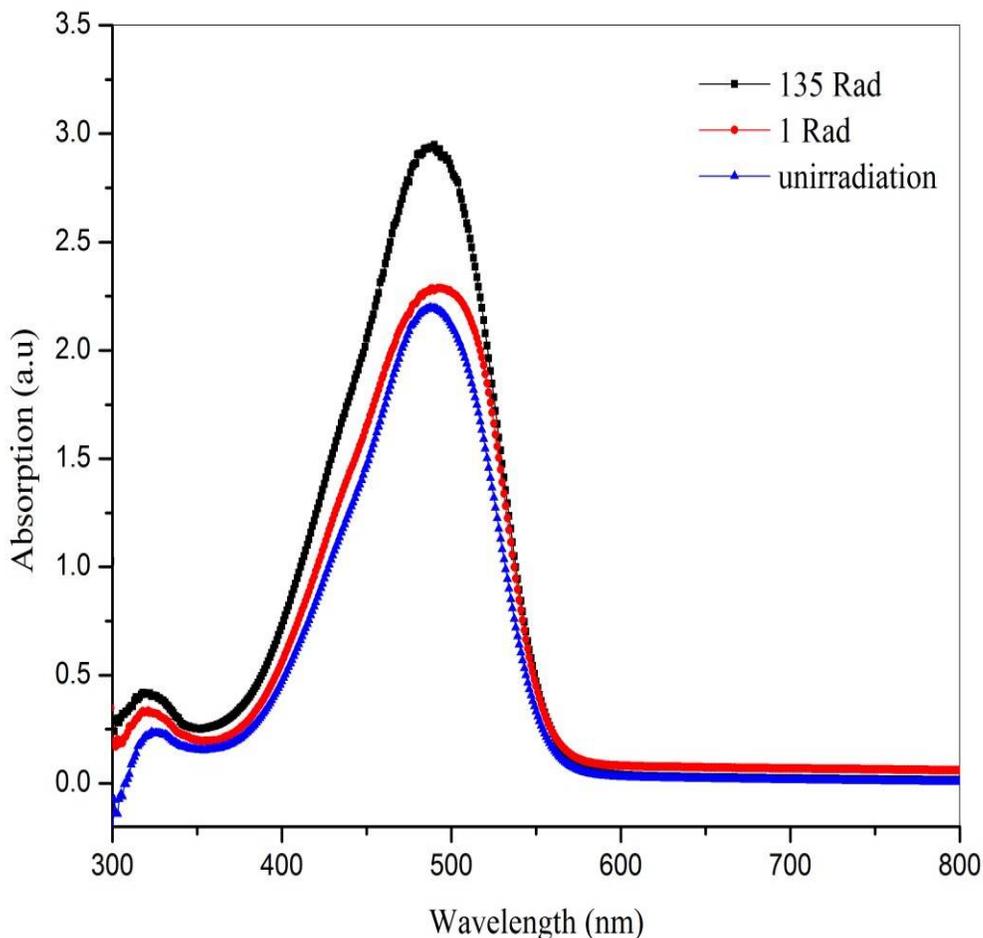


Figure (2): Absorption spectrum of of PMMA doped by BCG dye thin films before and after irradiation.

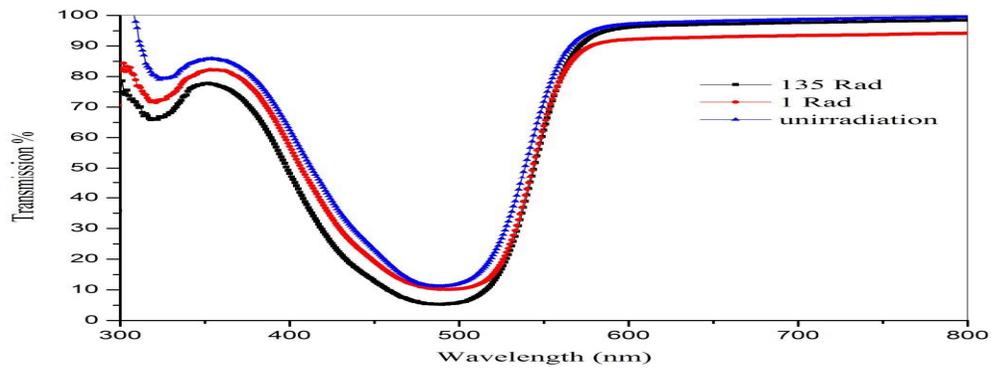


Figure (3): Transmittance spectrum of PMMA doped by BCG dye thin films before and after irradiation.

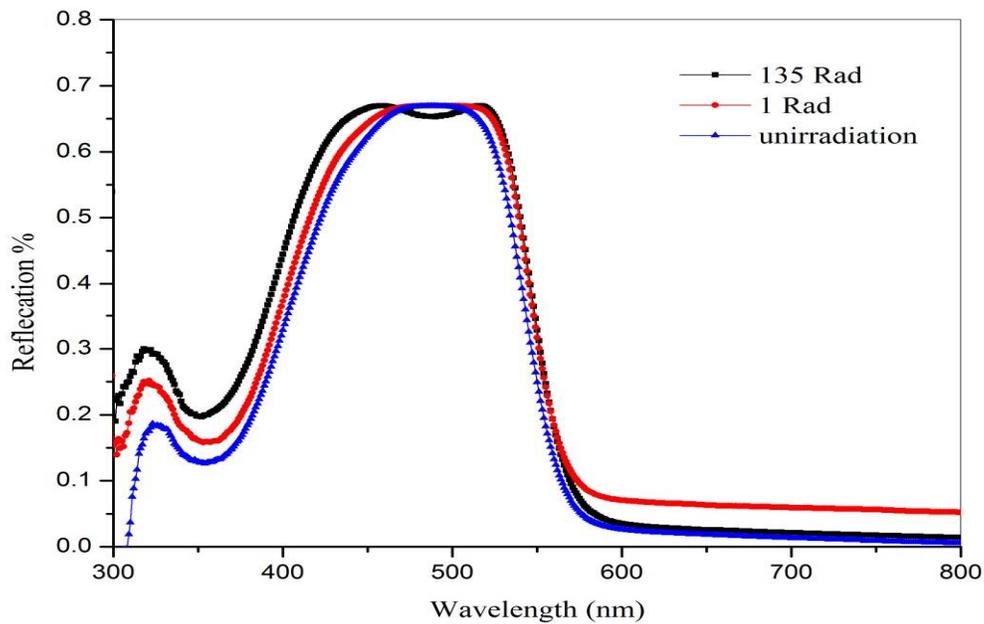


Figure (4): Reflection spectrum of PMMA doped by BCG dye thin films before and after irradiation.

The optical constants such as refractive index (n) and extinction coefficient (k) can be calculated by the equations [11]

$$n = \frac{\sqrt{R+1}}{\sqrt{R-1}} + \sqrt{\frac{4R}{R-1}} \quad (2)$$

$$k = \frac{2.303}{\lambda} \log_{10} \left(\frac{I_0}{I} \right)$$

(∞ -R) ∞

(3)

Where α is absorption coefficient and given by

$$\alpha = 2.303A/t \quad (4)$$

where t is the thickness of thin film, and λ is the wavelength of incident light (nm).

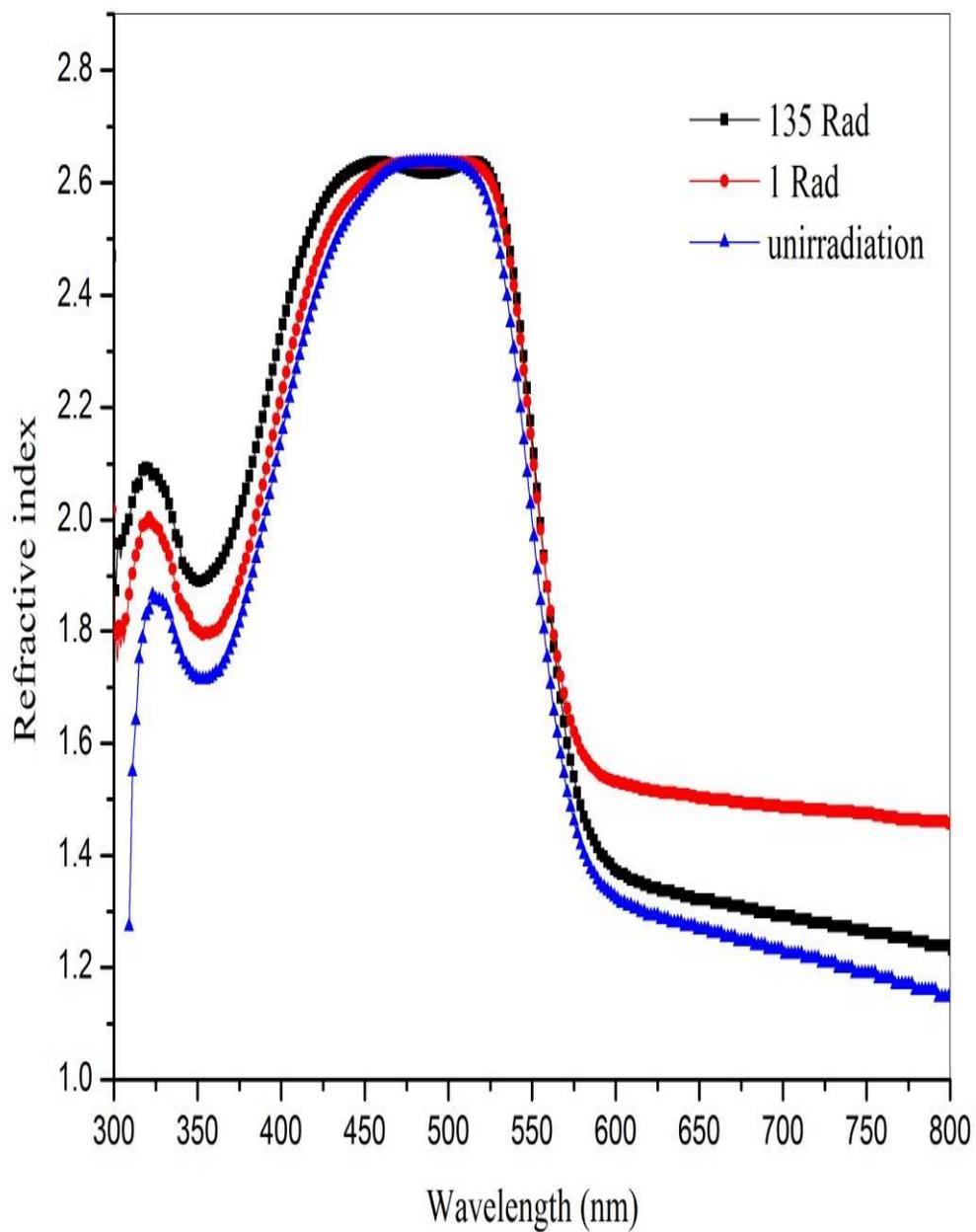


Figure (5): Refractive index of PMMA doped by BCG dye thin films before and after irradiation.

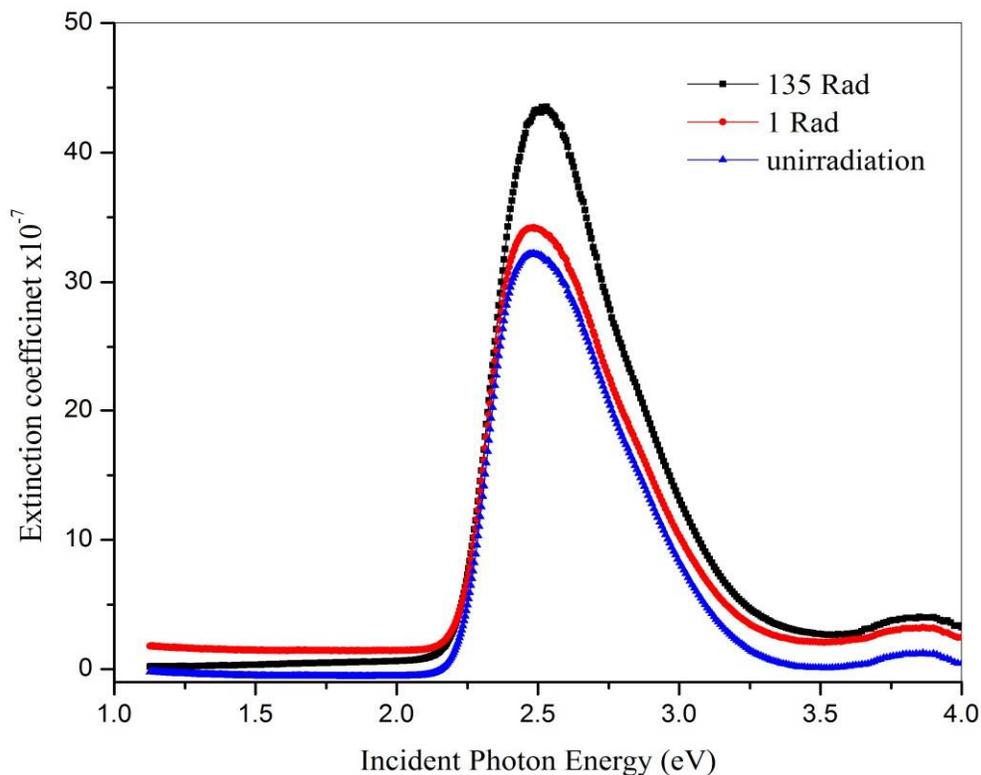


Figure (6): Extinction coefficient of PMMA doped by BCG dye thin films before and after irradiation.

Figures(5)and(6)showsthe refractiveindex(n)andextinctioncoefficient(k)ofofPMMA dopedby

BCGdye thinfilmsbeforeandafter irradiation,respectively.Theincrease ofnvalues withincreasing thedose irradiationled to increaseabsorbanceandmakethefilmsdenser,whichinturndecreased propagationvelocityoflight throughthemresultingto increase(n)values.While(n) represents the ratio oflightvelocitythroughvacuumtovelocitthroughany material.Then,thetmaterialbecome moreopaquet to the incident lights thus the velocity of light decreases and consequently n and k increases [7][12].This resultindicates that theirradiationofPMMA-BCG thin film willchange in the structure of the host-guest polymer- dye [17]. The irradiation has increased the absorbance in the visible regionInaddition;theopticalconductivity($\sigma_{optical}$) andelectricalconductivity canbe obtained fromthe equationsas[11]

$$n\alpha$$

$$\sigma_{optical} = \frac{n\alpha}{\pi} \quad (5)$$

$$\frac{4}{\pi}$$

$$\sigma_{electrical} = 2\lambda\sigma_{optical}/\alpha \quad (6)$$

The optical and electrical conductivity of PMMA doped by BCG dye thin films before and after irradiation is shown in figure (7), and (8) in which an increase in optical conductivity with increasing the irradiation dose was observed.

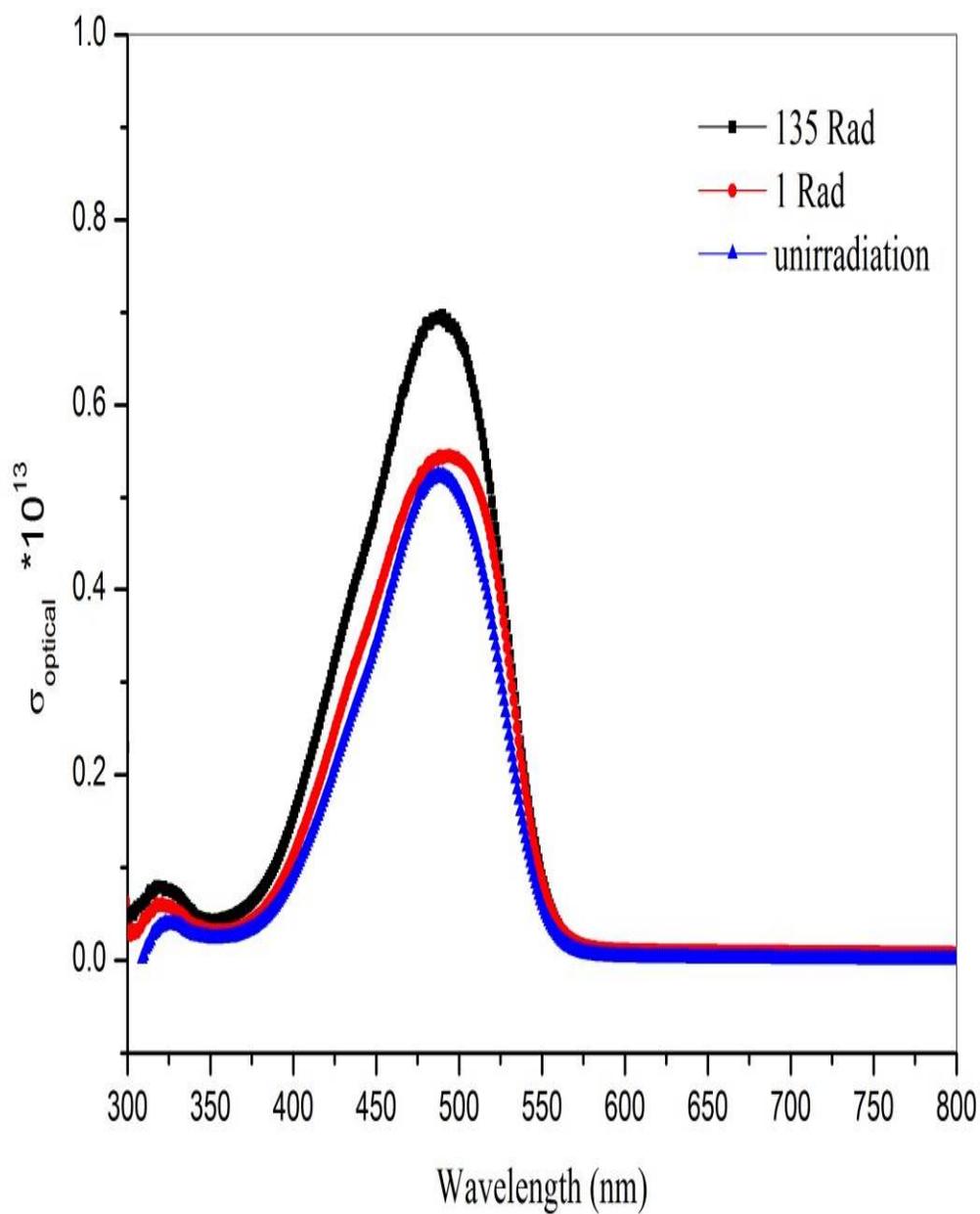


Figure (7): The optical conductivity of PMMA doped by BCG dye thin films before and after irradiation.

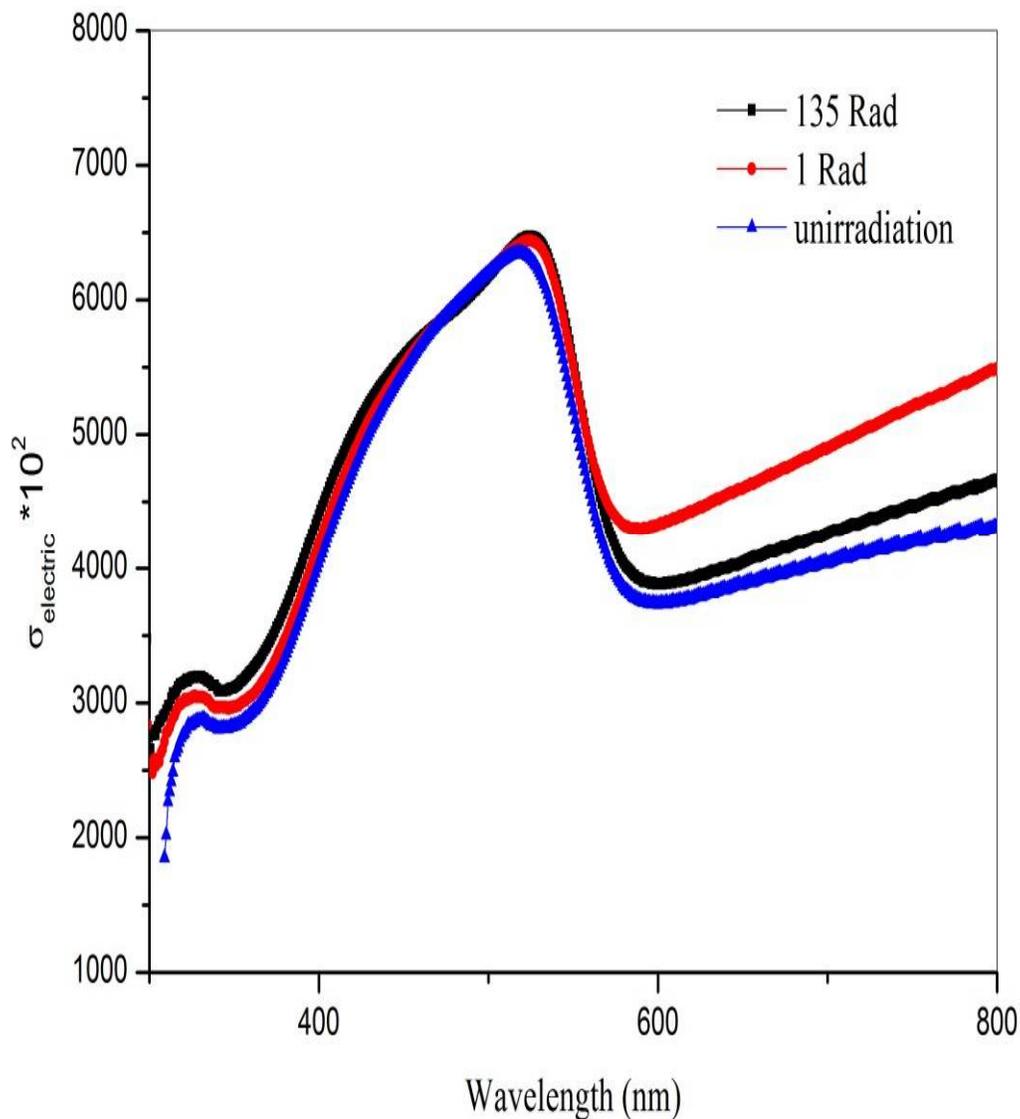


Figure (8): The electrical conductivity of PMMA doped 3% by BCG dye thin films before and after irradiation.

The absorption coefficient (α) as a function of the wavelength were calculated from the equation (4) and shown in figure (8), it can be clearly observed that the absorption is relatively small at long wavelengths. In addition, the absorption coefficient helps to conclude the nature of electronic transitions. When the high absorption coefficient values ($\alpha > 120 \text{ cm}^{-1}$) at higher energies, we expected direct electronic transitions, and the energy and momentum preserve of the electron and photon. Whereas the values of absorption coefficient is low ($\alpha < 120 \text{ cm}^{-1}$) at low energies, we expected indirect electronic transitions [13][4]. In our results, the value of α for all samples less than 120 cm^{-1} , so that the indirect electronic transitions will be deduced.

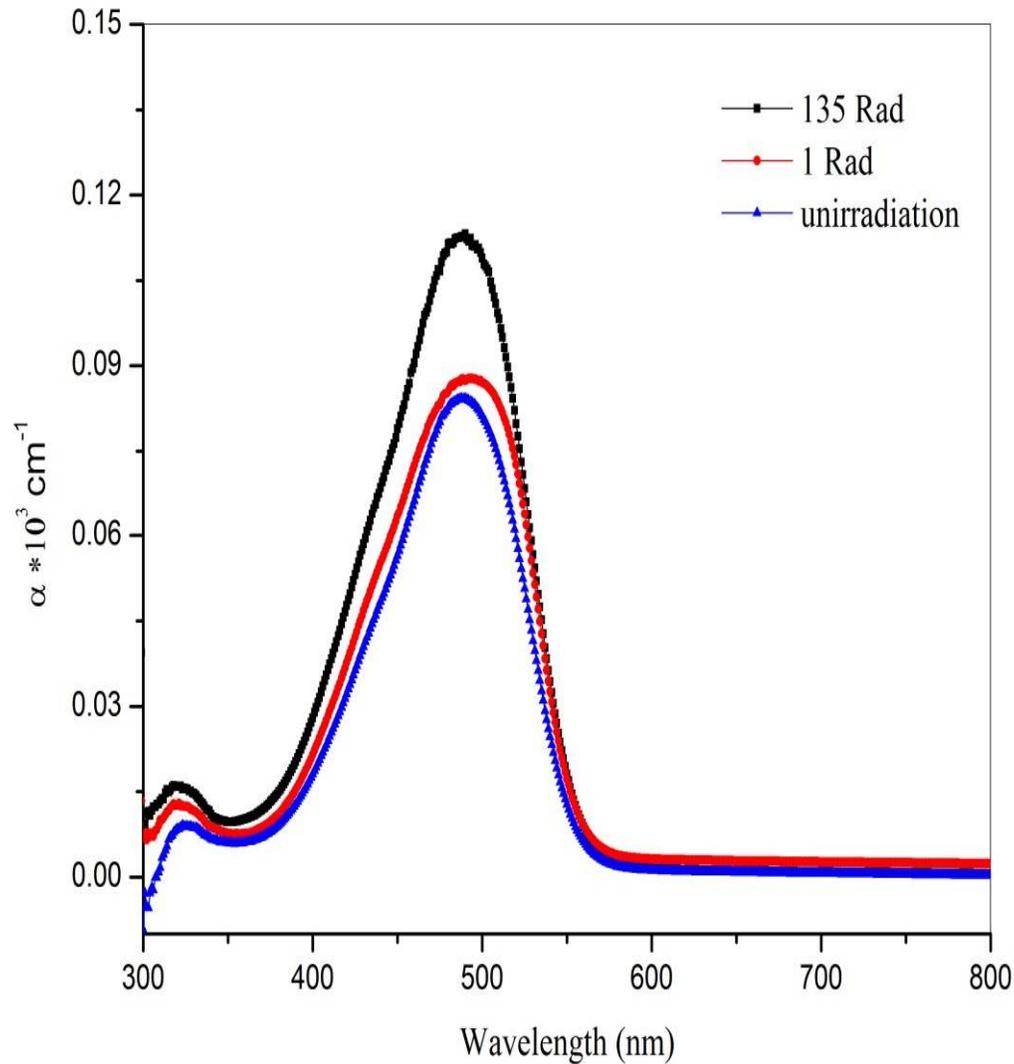


Figure (9): Absorption coefficient of PMMA doped by BCG dye thin films before and after irradiation.

Finally, from the absorption spectrum of PMMA-BCG film the optical energy band gap (E_g) was calculated by the Tau relation [9]

$$\alpha h\nu = B(h\nu - E_g^{opt})^r \quad (6)$$

Where B is a constant, and depends on type of material, ν is the frequency of incident light, and r is the exponential constant, its value depends on the type of transition, where $r = 1/2$ for allowed direct transition, $r = 3/2$ for the forbidden direct transition, $r = 2$ for allowed indirect transition, and $r = 3$ for the forbidden indirect transition.

Figure (10) shows the optical indirect energy gap (E_g indirect) values which was calculated by the evaluation of the straight line of $(\alpha h\nu)^{1/2}$ plot against photon energy in the high absorption range followed by extrapolating the linear region of the plot to $(\alpha h\nu)^{1/2} = 0$. The indirect energy gap of the PMMA-BCG film before irradiation was found to be equal to 2.1 eV, as shown in figure (10), and this value begins to decrease to 2.08 eV and 2.04 eV respectively, after irradiation. This decrease can be attributed to the creation of the

site levels in forbidden indirect energy gap leading to facilitate the crossing of electron from the valence band to the local levels to conduction band [14– 16]

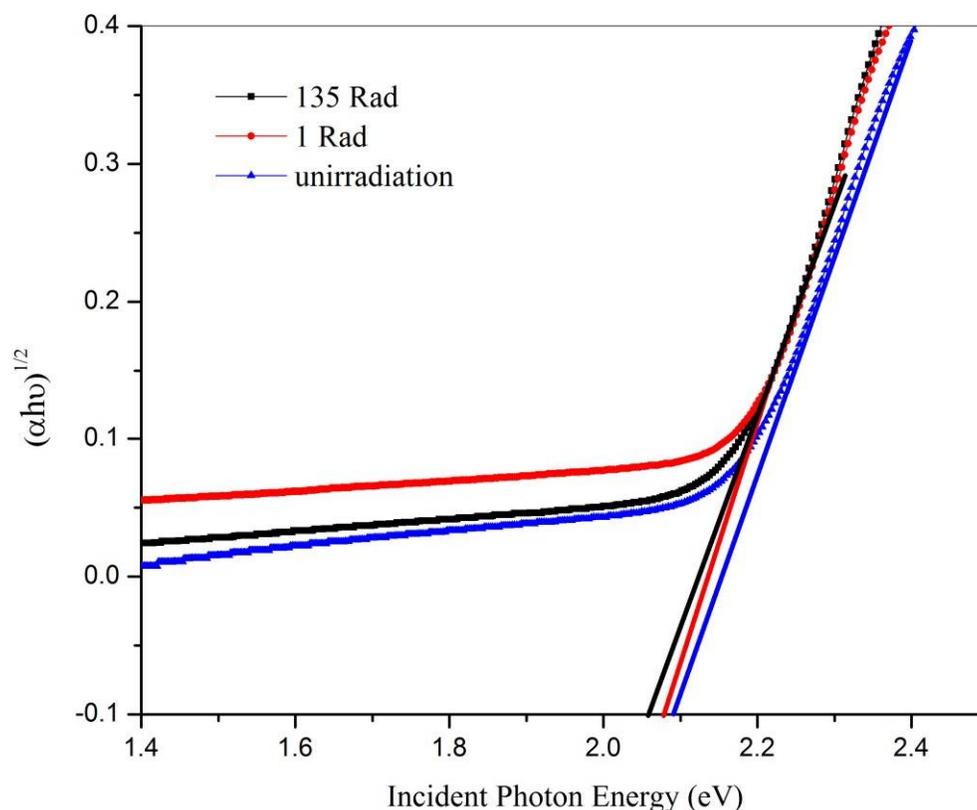


Figure (10): Indirect energy gap PMMA doped by BCG dye thin films before and after irradiation.

CONCLUSION

In this experimental study, we have investigated the effects of Gamma irradiation on the optical properties of PMMA-BCG thin films. Using absorption and transmittance spectrum for samples before and after irradiation, the optical constant such as absorption coefficient, refractive index, extinction coefficient, and optical conductivity, have been studied. Irradiation dose increment effect in the structure of film led to enhance the optical properties of PMMA-BCG, while the irradiation dose increment in the structure of PMMA-BCG film has been led to small decreasing in the band gap of film. Therefore, it can be concluded that the BCG/PMMA thin films consider a promising material for diverse meter application.

REFERENCES

- [1] "Osswald · Baur · Brinkmann Oberbach · Schmachtenberg International Plastics Handbook," 2015.
- [2] S. P. Gault, B., Moody, M.P., Cairney, J.A., and Ringer, Springer Series in Materials Science. 2012.
- [3] D. M. Rück, "Ion induced modification of polymers at energies between 100 keV and 1 GeV applied for optical waveguides and improved metal adhesion," Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms, vol. 166, pp. 602–609, 2000.
- [4] V. Ghorbani, M. Ghanipour, and D. Dorrani, "Effect of TiO₂/Au nanocomposite on the optical properties of PVA film," Opt. Quantum Electron., vol. 48, no. 1, pp. 1–14, 2016.
- [5] J. Davenas, "By Ion Beam Irradiation," Science (80-.), 1990.

- [6] A. Bhattacharya, "Radiation and industrial polymers," *Prog. Polym. Sci.*, vol. 25, no. 3, pp. 371–401, 2000.
- [7] A. Abu El-Fadl and A. M. Nashaat, "Gamma-ray irradiation effects on the optical properties of KHSO₄ single crystals," *Radiat. Eff. Defects Solids*, vol. 170, no. 11, pp. 863–875, 2015.
- [8] U. Ali, K. J. B. A. Karim, and N. A. Buang, "A Review of the Properties and Applications of Poly (Methyl Methacrylate) (PMMA)," *Polym. Rev.*, vol. 55, no. 4, pp. 678–705, 2015.
- [9] E. H. Lee, "Ion-beam modification of polymeric materials - fundamental principles and applications," *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms*, vol. 151, no. 1–4, pp. 29–41, 1999.
- [10] Indranil Mitra, Gopa Roy Biswas And Sutapa Biswas Majee. "Effect of Filler Hydrophilicity on Superdisintegrant Performance and Release Kinetics From Solid Dispersion Tablets of A Model BCS Class II Drug." *International Journal of Pharmacy Research & Technology* 4.2 (2014), 28-33..
- [11] Hesaraki, M. "Diarrhea in infants", (2018) *International Journal of Pharmaceutical Research*, 10 (1), pp. 143-146.
- [12] K. Makuuchi and S. Cheng, *Radiation Processing of Polymer Materials and its Industrial Applications*. 2011.
- [13] Siddhartha, S. Aarya, K. Dev, S. K. Raghuvanshi, J. B. M. Krishna, and M. A. Wahab, "Effect of gamma radiation on the structural and optical properties of Polyethyleneterephthalate (PET) polymer," *Radiat. Phys. Chem.*, vol. 81, no. 4, pp. 458–462, 2012.
- [14] T. J. Alwan, "Gamma irradiation effect on the optical properties and refractive index dispersion of dye doped polystyrene films," *Turkish J. Phys.*, vol. 36, no. 3, pp. 377–384, 2012.
- [15] S. Eid, S. Ebraheem, and N. M. Abdel-Kader, "Study the Effect of Gamma Radiation on the Optical Energy Gap of Poly(Vinyl Alcohol) Based Ferrotitanium Alloy Film: Its Possible Use in Radiation Dosimetry," *Open J. Polym. Chem.*, vol. 04, no. 02, pp. 21–30, 2014.
- [16] R. Qindeel, "Effect of gamma radiation on morphological & optical properties of ZnO nanopowder," *Results Phys.*, vol. 7, pp. 807–809, 2017.