Optical Properties of Sudan Black Stain Doped PMMA Thin Films at Different Concentration and Gamma Irradiation Effect

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Abstract

In this paper, the optical properties investigated and the effect of the gamma irradiation on the optical constant in addition to the energy band gap (E_g) of Sudan black stain doped Poly Methyl Methacrylate (PMMA) thin films. Thin films of 20% Sudan black stain/PMMA doping ratio was used to prepared three concentrations (1, 0.7, 0.4) x10^{-3} M. all the Dye/ Polymer solution (three different concentrations) deposited on glass substrate by using a free casting method at room temperature. The UV-Visible absorbance and transmittance spectra at the 300 - 800 nm wavelength range were used to investigate the optical properties of the films. The optical constant such as linear absorption coefficient, the extinction coefficient, and E_g were calculated. Results showed an increasing in the optical properties after irradiation with γ rays with activity 16 gray/hour, while E_g was decreasing after irradiation.

Key Words: Dye Doped Polymer, Optical Constants, Gamma Ray Effect.

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Introduction

Polymers have been extensively investigated owing to their applications in modern optical devices.so; the study of optical properties of polymer materials has attracted the attention of researchers. Especially, it has unique and distinctive properties. Such as low density, low cost Compared with the other optical materials types and high flexibility (Shima zahedi and et al., 2013) One of the important and interesting polymer is Poly methyl methacrylate (PMMA), according to his attractive optical properties. PMMA contains both hydrophobic (methylene) and hydrophilic (carbonyl) groups in each unit. As a polymer waveguide, PMMA has attracted a lot of interest for its use in optical instrument components and in optoelectronic devices due to its low cost and ease of fabrication and forming. In addition, it was found that it can produce a significant difference in refractive index compared to acrylamide-based photopolymers (Essam Abdel–Fattah., 2019).

When the electron excitation from the valence band (V-band) to the conduction band (C-band) generated a pair of hole electrons, this process are called the fundamental absorption, it is the most important process to determining the fundamental absorption edge. Therefore, these processes are called band to band transitions. If the wavelength of the incident photon coincides with the absorption edge, then the E_g relationship can be obtained through the equation (Al-Kadhemy and et al. 2013).

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The fundamental absorption occurred when,

$$E_g = \Delta E = h\upsilon = \frac{hc}{\lambda} \quad (1)$$

The Eg (eV) of materials are obtained from optical transmission. In addition, linear absorption coefficient (α) of thin films can be calculated from the relation:

$$\alpha = \frac{1}{t}\ln\left(\frac{1}{T}\right) \quad (2)$$

Where the thickness of the film is (t) and T is the transmittance the film at the same wavelength, there is a relationship between the absorption coefficients α (Cm^{-1}) and the incident energy hυ (eV) is calculated by (Rashid and et al. 2013):

$$(\alpha h\upsilon)^{1/n} = A(h\upsilon - E_g) \quad (3)$$

Where A is a constant, and exponent n depends on the transition type, where n=2, for indirect allowed transition, and n=1/2, for direct allowed transition, while n=3, for indirect forbidden transition, and n=3/2, for direct forbidden transition (Abd AL Rasheed and et al. 2013).

The extinction coefficient which is defined The decay coefficient is defined as the amount of energy loss experienced by the electromagnetic wave when it passes through the optical material, and it is related with the wavelength and the linear absorption coefficient by the following relationship (Sönmezoglu and et al. 2015):

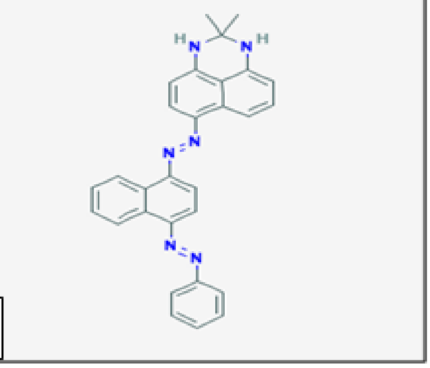
$$K = \frac{\lambda\alpha}{4\pi} \quad (4)$$

Materials and Samples Preparation

Sudan black stain dye Purchased from (Sigma-Aldrich). The dye molecular formula $C_{29}H_{24}N_6$ and its chemical structure is depicted in Figure (1a). Sudan dyes Sudan dye is one of the organic dyes and has many industrial uses as it is used in plastic colorants as well as, used in biological applications in coloring biological samples. It is worth noting that one of the most important features of this family of dyes is that they are well soluble in fats and alcohol, so they are used industrially in the coloring of plastics (*Gerald*. 2000). Poly methyl methacrylate (PMMA) polymer was purchased from (Sigma-Aldrich) and the molecular formula of PMMA is $(C_5O_2H_8)$n. the figure (1b) are shown the chemical structures for PMMA (Almusawe and et al. 2018). It is a type of thermoplastic polymer distinguished by its high transparency, so it is also called acryl glass or plexiglass, as the latter is the first commercial name that was put on the market in 1933; There are also several trade names for it. The repeating unit in this polymer consists of methyl methacrylate, where the polymerization process is carried out according to the radical method. PMMA is used as host material for dye according the his good optical properties (Huseynova. 2020).

2.5 g from PMMA powder dissolved in 25 ml chloroform with magnetic stirrer for 3 hours to prepare the polymer solutions by the same procedure for dye solution. The (PMMA/Sudan black) mixtures solution with 1 mM and placed on a magnetic Stirrer for 1 hour to ensure the solution have good homogeneity. after that By using equation M1V1=M2V2 we are prepared the other concentrations from dye/polymer solution (Beiser. 2008). Then the solution casted on a clean glass plate washed with acetone and distilled water. Finally, the films were left to dry in room temperature for 24 hours. The thin films with thickness about 55-60 μm were obtained.

The absorption spectrum of the prepared films were investigated by UV-Vis spectrophotometer in the range 300-800 nm. Then, Sudan black/PMMA samples with different concentration (1, 0.7, 0.4) mM, respectively, with size 3 * 1 cm were cut from the commercially available glass sheet. These samples subjected to irradiation using 60Co Gamma source with 16 gray/hour activity.

a


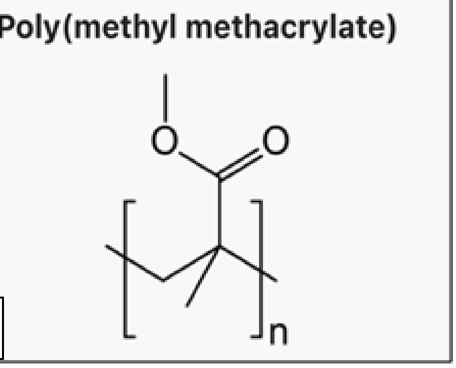
b


Figure 1. Chemical structure of (a) Sudan black stain, (b) pmma

Results and Discussion

Transmittance (T) and Absorption (A) spectrum were given in the figures (2 a-b) and (3 a-b) for Sudan black/PMMA film measured by UV-Vis spectrophotometer for the irradiated and non-irradiated samples at different concentration (1, 0.7, 0.4) mM. The absorbance spectra as a function of the wavelength of the incident light for PMMA- Sudan black film are shown in Figure (2 a). As it is clear, an increase in the absorbance of the doped polymer than the pure polymer, as well as increase absorption with increased doped concentration due to the addition of Sudan black stain this behavior are the same to result in reference (Huseynova. 2020, Andam and et al. 2021). From the fig (2 b) after irradiation with γ rays with activity 16 gray/hour, we notice an increase in the absorption spectrum for pure PMMA and by doped with Sudan black stain the absorption more increase with increasing the concentration this matches with the results of (Abd El-Rahman, 2019, Darwish and et al. 2016).

The transmittance spectra appear in Figure (3 a) before irradiation where the increase in concentration doped with the Sudan black stain caused decrease in transmittance spectra because the increasing in doping concentrations of the dye caused increasing in the light absorption. While the transmission spectra for pure and doped polymer after irradiation with γ rays appear in Fig. (3-2 b) where the value of transmission decrease than before irradiation for pure PMMA, then it's gradually less more with increasing stain concentration at (0.4, 0.7, 1) mM.

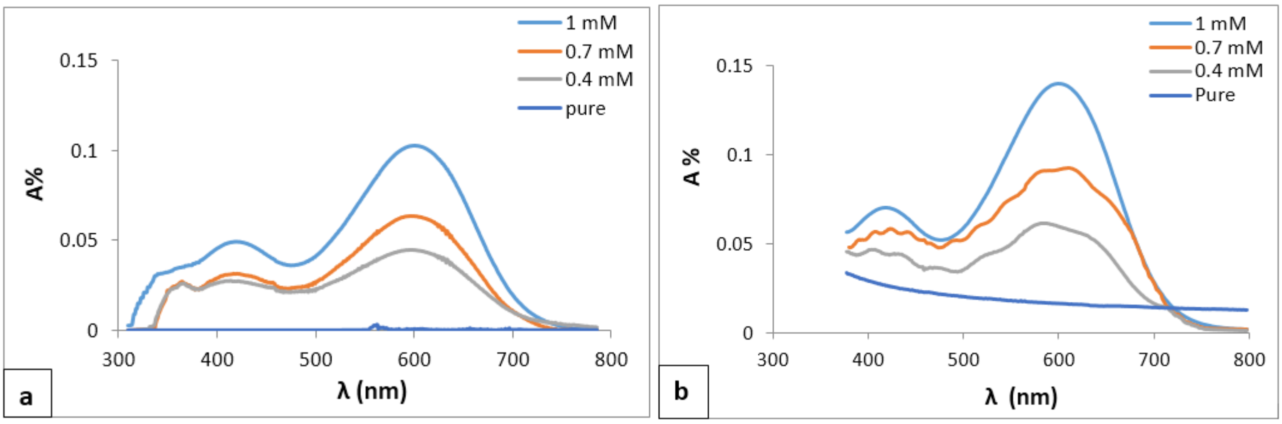


Fig. 2. Absorbance as a function of the wavelength of pure and doped polymer. a: before irradiation. b: after irradiation with γ rays

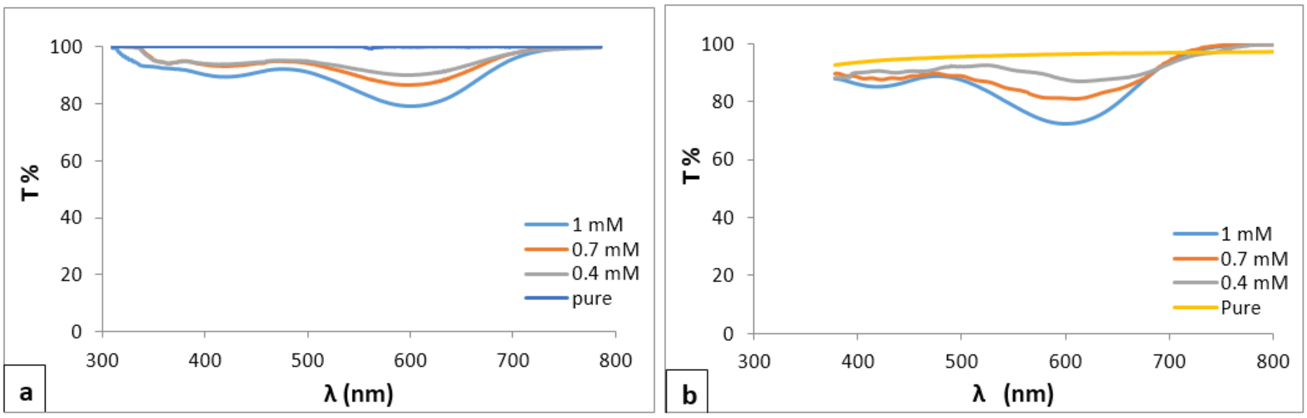


Fig. 3. Transmission as a function of the wavelength of pure and doped polymer. a: before irradiation. b: after irradiation with γ rays

The absorption coefficient (α) and Extinction coefficient (k) are calculated from the equation (2), (4), respectively. And shown in Figure (4 a-b) and (5 a-b) before and after irradiation at different concentration (1, 0.7, 0.4) mM, respectively.

Fig (4 a) and fig (5 a) represent α and k before irradiation where they increase with increasing wavelength, due to decreasing the transmission reach to (600) nm. Then they returns to decrease. Through the figures, note that the value of α and k increases when the polymer (PMMA) doped with

Sudan black stain than pure PMMA, and this value increases by increasing the concentration ratio.

Fig (4 b) and fig (5 b) represent the absorption coefficient and Extinction coefficient after irradiation with γ rays with activity 16 gray/hour. Fig (4 b) its appear a clear increase in the values of the absorption coefficient of the pure and doped polymer due to the decrease in the transmittance values. While from fig (5 b) notice increase in the values of the extinction coefficient of the pure and doped polymer due to the increase in the absorption coefficient values where the direct relationship between them.

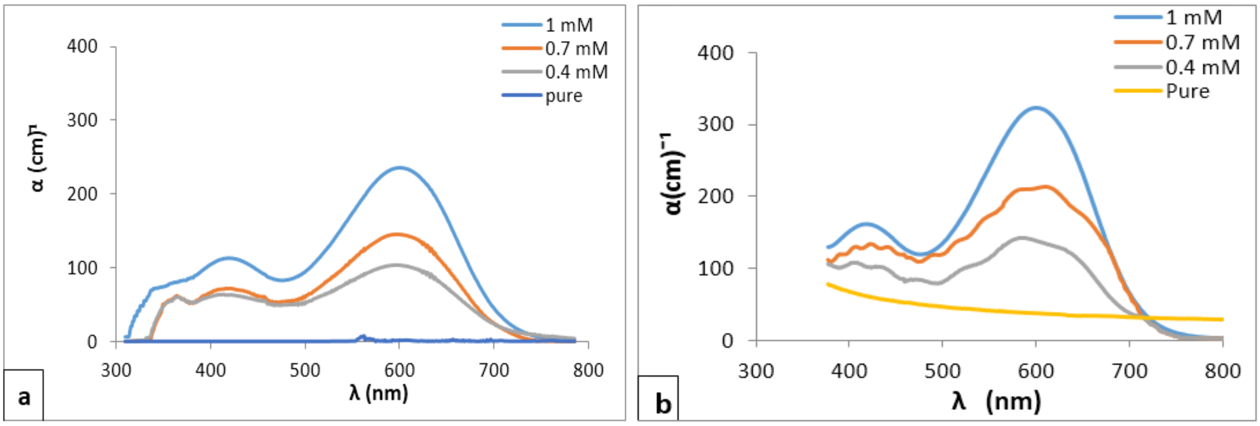


Fig. 4. Absorption coefficient as a function of the wavelength of pure and doped polymer. a: before irradiation. b: after irradiation with γ rays

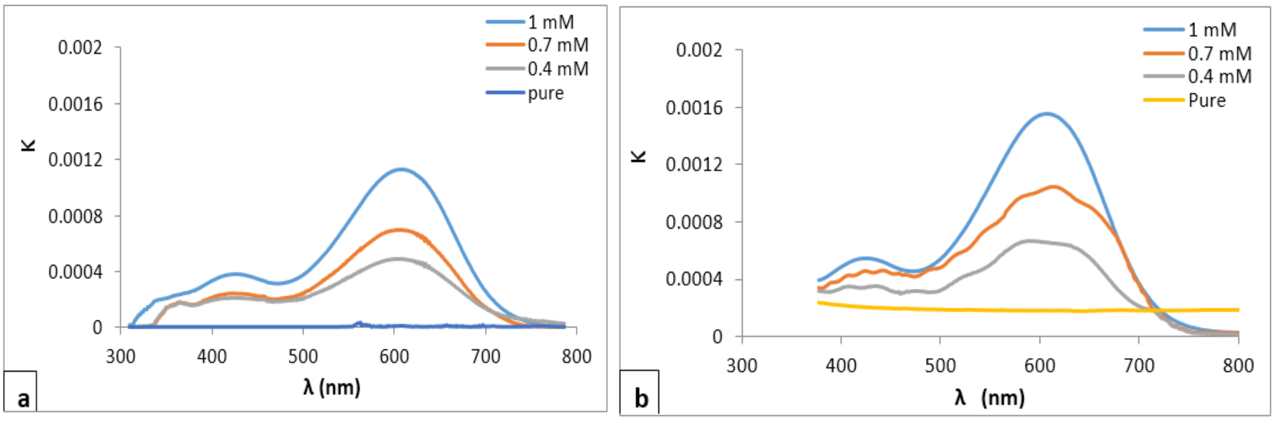


Fig. 5. Extinction coefficient as a function of the wavelength of pure and doped polymer. a: before irradiation. b: after irradiation with γ rays

The direct and indirect energy gap of pure polymer (PMMA) before irradiation was measured and it was found to be equal to (3.9, 3.2) eV, respectively, shown in Figure (6), and that these values start decreasing to (1.83, 1.75) eV when doped the polymer with Sudan black stain at a concentration of (0.4) mM in figure (7). By increasing the dye concentration the the Eg_d and Eg_{in} will gradually decreasing in Fig. (8) and Fig. (9), all these values represent in table (1).

After irradiation with γ rays there was a decreases can be observed in the value of energy gap for irradiated polymer in Fig. (10), and irradiated doped (PMMA-Sudan black) film at (0.4, 0.7, 1) mM as show in figures (11), (12), (13) respectively, and indicated in the table (2).

Table 1. Represent the values of Eg_d and Eg_{in} of pure and doped polymer before irradiation

Before irradiation	Eg_d (eV)	Eg_{in} (eV)
Pure PMMA	3.9	3.3
PMMA- Sudan black 0.4 mM	1.83	1.75
PMMA- Sudan black 0.7 mM	1.82	1.74
PMMA- Sudan black 1mM	1.81	1.72

Table 2. Represent the values of Eg_d and Eg_{in} of pure and doped polymer before irradiation after irradiation with γ rays

After irradiation	Eg_d (eV)	Eg_{in} (eV)
Pure PMMA	2.7	2.3
PMMA- Sudan black 0.4 mM	1.79	1.72
PMMA- Sudan black 0.7 mM	1.77	1.70
PMMA- Sudan black 1mM	1.76	1.66

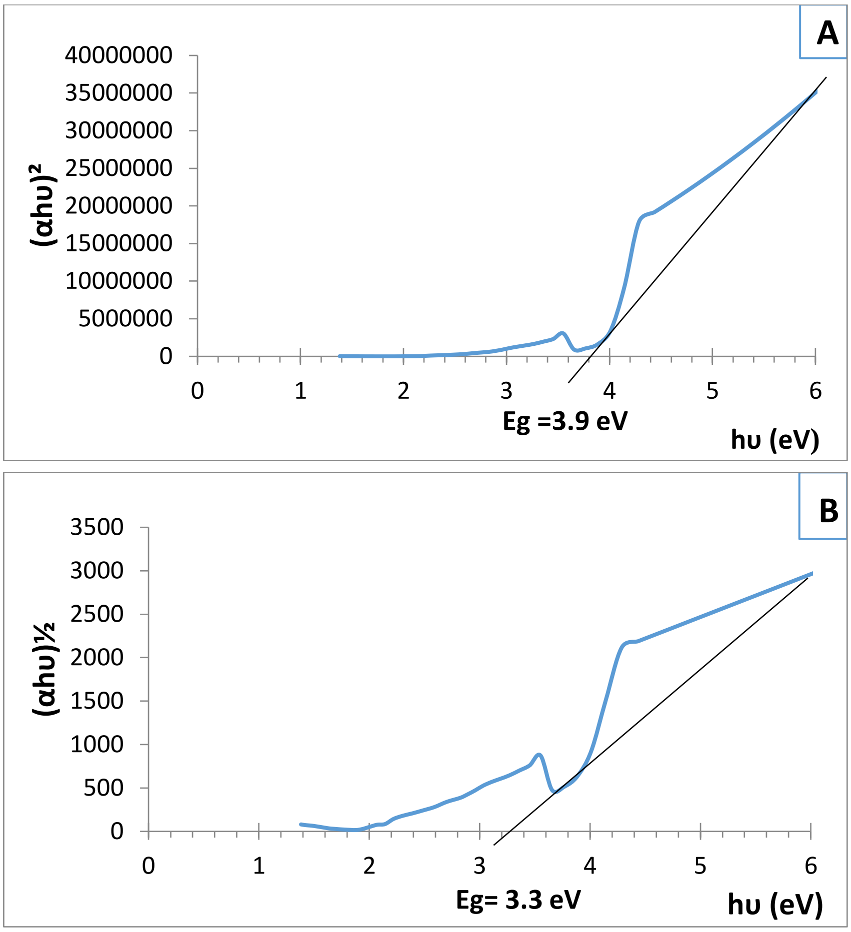


Figure 6. A: the direct energy gap, B: the indirect energy gap of the pure polymer before irradiation

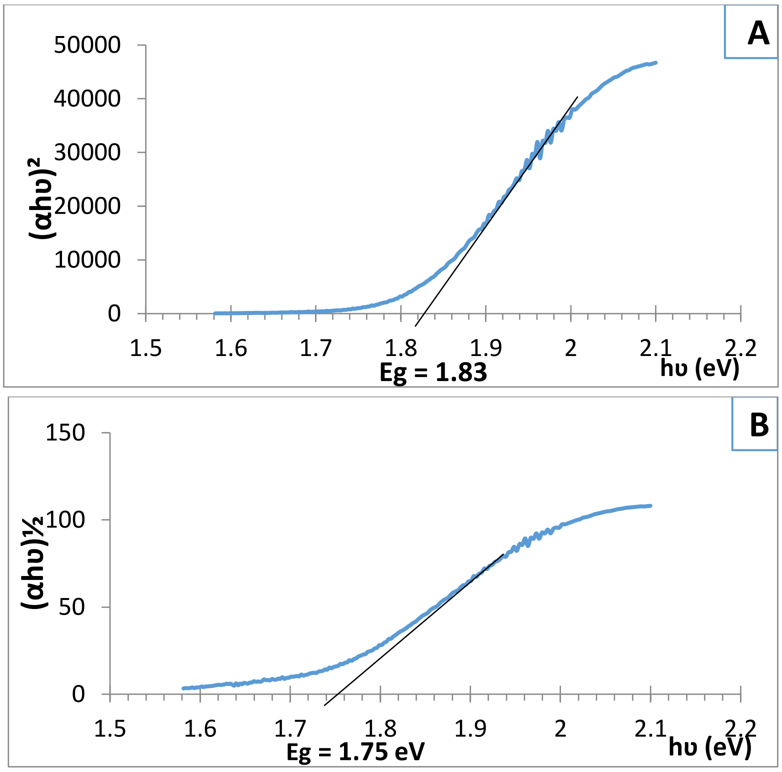


Figure 7. A: the direct energy gap, B: the indirect energy gap of the PMMA polymer doped with Sudan black stain at a concentration of 0.4 mM before irradiation

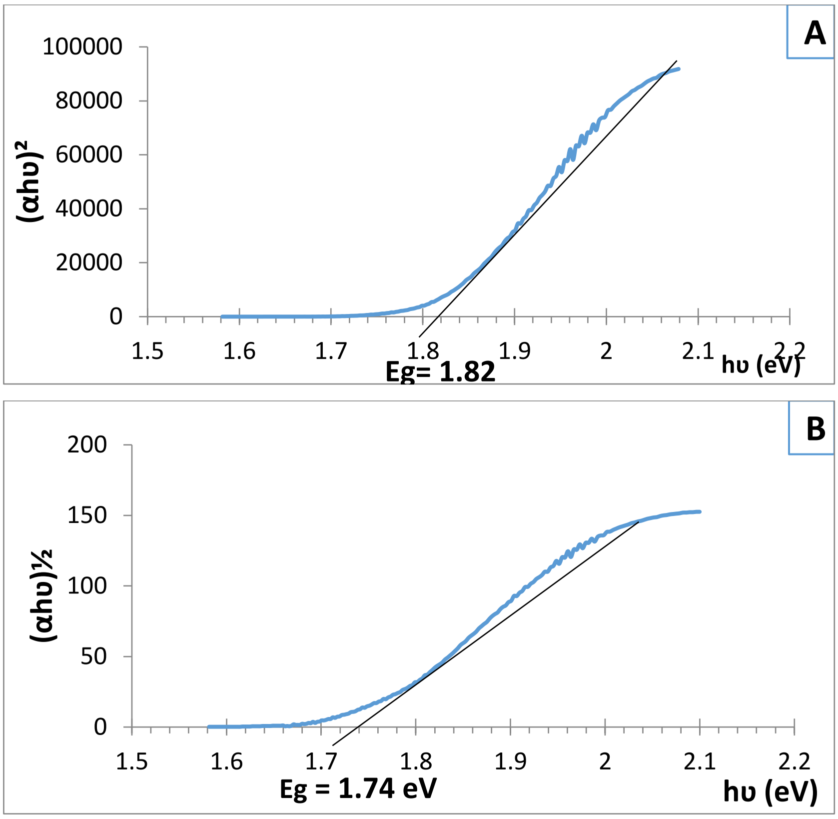


Figure 8. A: the direct energy gap, B: the indirect energy gap of the PMMA polymer doped with Sudan black stain at a concentration of 0.7 mM before irradiation

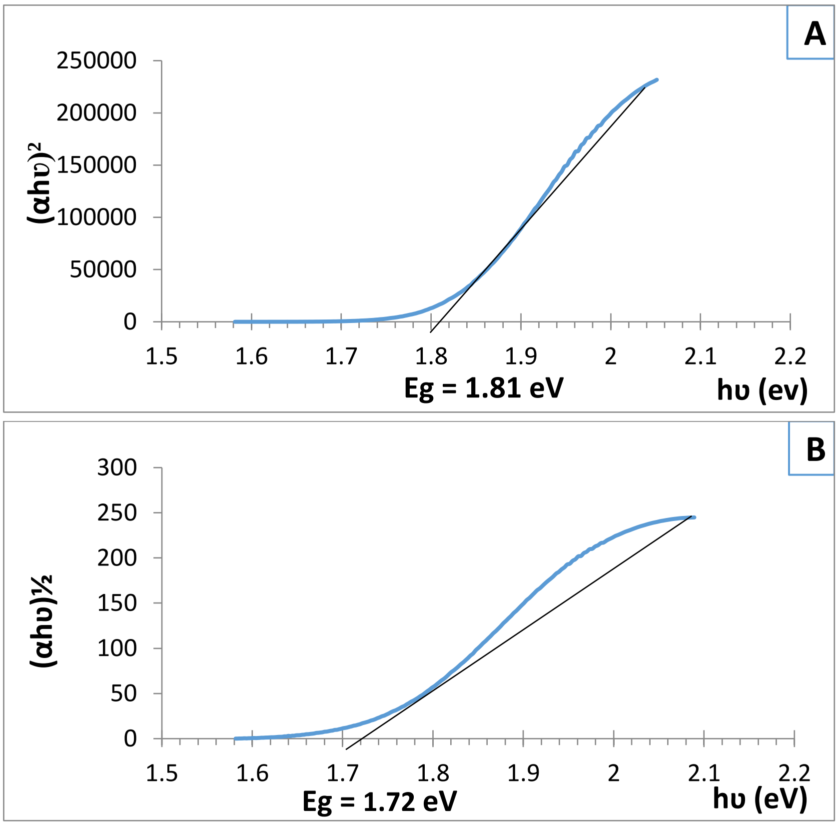


Figure 9. A: the direct energy gap, B: the indirect energy gap of the PMMA polymer doped with Sudan black stain at a concentration of 1 mM before irradiation

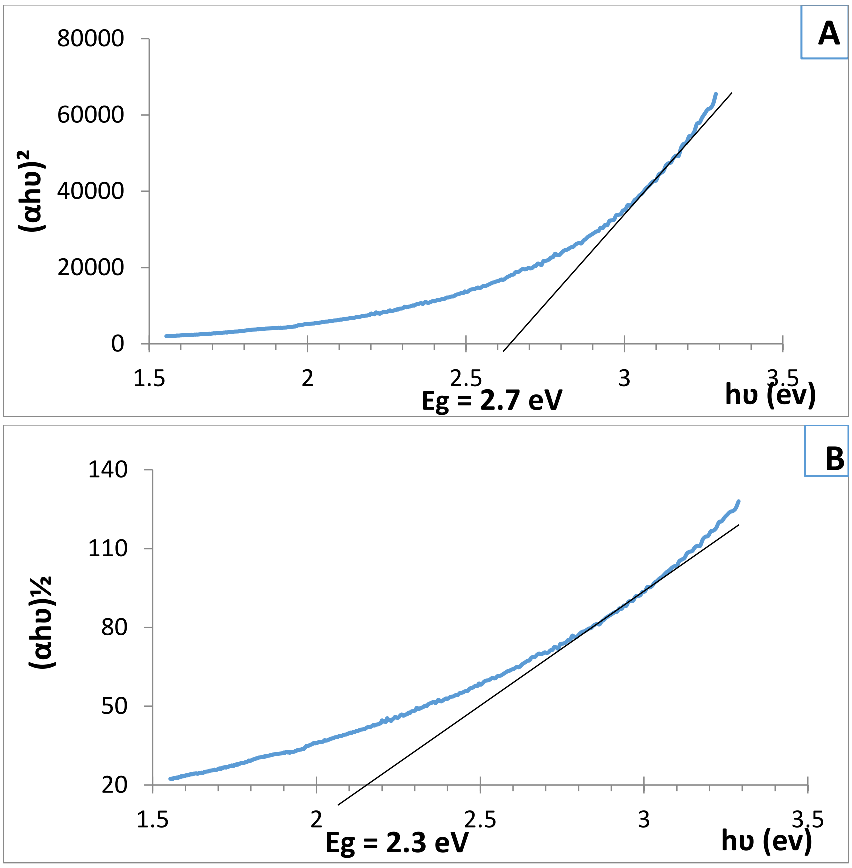


Figure 10. A: the direct energy gap, B: the indirect energy gap of the pure polymer after irradiation with γ rays

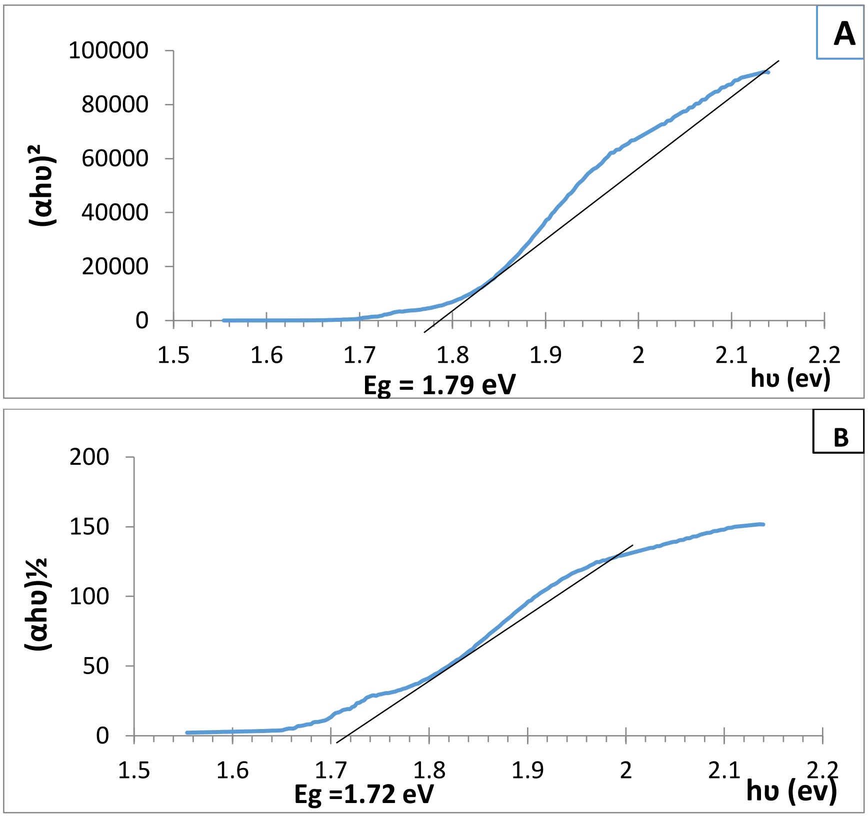


Figure 11. A: the direct energy gap, B: the indirect energy gap of the PMMA polymer doped with Sudan black stain at a concentration of 0.4 mM after irradiation with γ rays

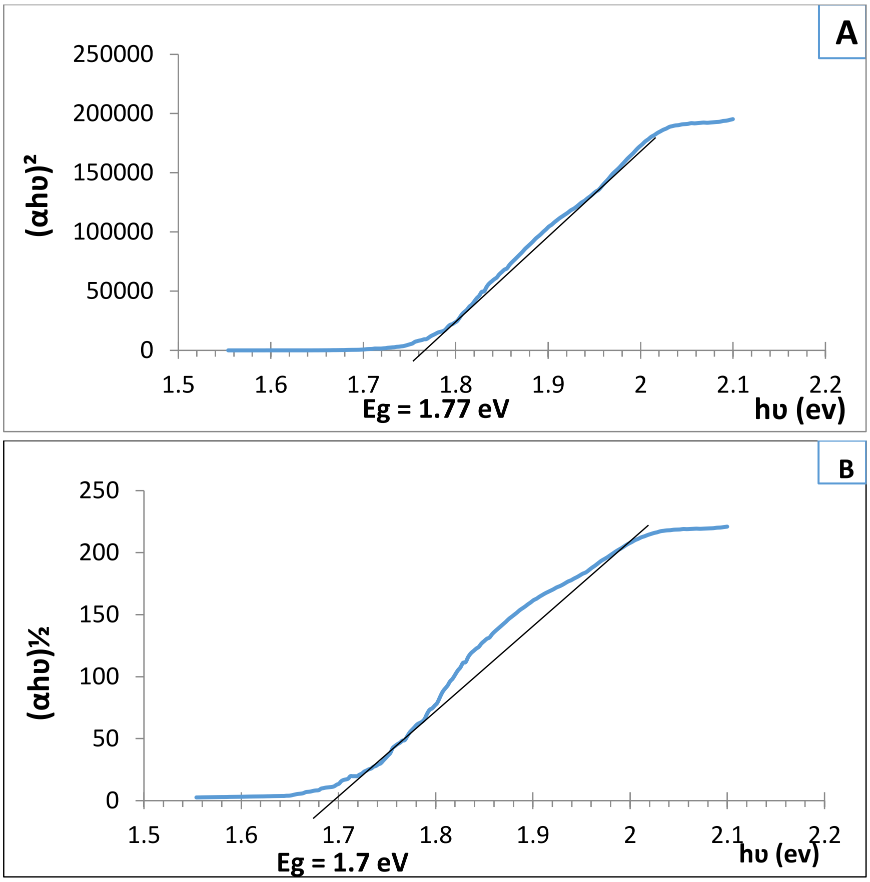


Figure 12. A: the direct energy gap, B: the indirect energy gap of the PMMA polymer doped with Sudan black stain at a concentration of 0.7 mM after irradiation with γ rays

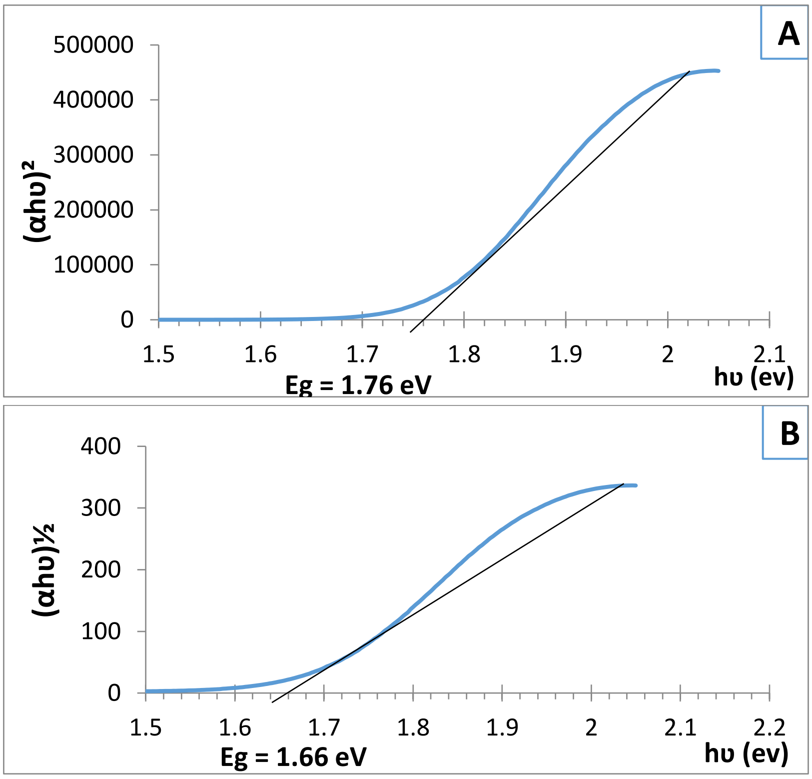


Figure 13. A: the direct energy gap, B: the indirect energy gap of the PMMA polymer doped with Sudan black stain at a concentration of 1 mM after irradiation with γ rays

References

Zahedi S, Dorranian D. Effect of laser treatment on the optical properties of poly (methyl methacrylate) thin films. *Optical review* 2013; 20(1): 36-40.

Abdel–Fattah E. Surface activation of poly (methyl methacrylate) with atmospheric pressure ar+h_2o plasma. *Coatings* 2019: 9(4).

Al-Kadhemy MH, Rasheed ZS. Effect of doping ratio on optical properties of coumarin doped polystyrene films. *International Journal of Application or Innovation in Engineering & Management* 2013; 2(8): 179-185.

Rashid FL, Hashim A, Habeeb MA, Salman SR, Ahmed H. Preparation of (PS-PMMA) copolymer and study the effect of Sodium Fluoride on its optical properties. *Science & Technology* 2013; 4(2): 121-126.

Rasheed NFAA. *Preparation and Characterization of annealed CAO/Si hetrojunction detectoe,* Ms.c thesis, University of Technology 2015.

Sönmezoğlu S, Arslan A, Serin T, Serin N. The effects of film thickness on the optical properties of TiO_2–SnO_2 compound thin films. *Physica Scripta* 2011: 84(6).

Booth G. *Dyes, General Survey,* Wenham: Wiley 2000.

Kadhum RJ, Almusawe AJ, Hassen TF. Study of Gamma irradiation effect on the Optical Properties of Bromocresol Green Dye Doped Poly Methyl Methacrylate Thin Films. *Eurasian Journal of Analytical Chemistry* 2018; 13(3): 336-348.

Almusawe AJ, Hassen TF, Rahma MA. Linear Optical Properties of Bromocresol Green Dye Doped Poly Methyl Methacrylate Thin Films. *Iraqi Journal of Science* 2018: 299-306.

Beiser A. *Concept of modern pysics,* Book, Tata McGraw-Hill publishing company, Inc 2008.

Huseynova G, Lee SH, Joo CW, Lee YS, Lim YJ, Park J, Lee JH. Dye-doped poly (3, 4-Ethylenedioxythiophene)-Poly (Styrenesulfonate) electrodes for the application in organic light-emitting diodes. *Thin Solid Films* 2020: 707.

Andam N, Refki S, Ishitobi H, Inouye Y, Sekkat Z. Optical Characterization of Ultra-Thin Films of Azo-Dye-Doped Polymers Using Ellipsometry and Surface Plasmon Resonance Spectroscopy. *In Photonics,* Multidisciplinary Digital Publishing Institute 2021: 8(2).

Abd El-Rahman M, Yassien KM, Yassene AA. Effect of gamma irradiation on the optical properties of epoxy resin thin films. *Optik* 2019; 183: 962-970.

Darwish AAA, Issa SA, El-Nahass MM. Effect of gamma irradiation on structural, electrical and optical properties of nanostructure thin films of nickel phthalocyanine. *Synthetic Metals* 2016; 215: 200-206.

Al-Sawaff ZH, Rashid ZM, Yahya YZ, Kandemirli F. Electromagnetic field smart splint for bone fixing and rehabitation using niti shape memory alloy. *NeuroQuantology* 2020; 18(3): 37-44.