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Study the Optical Properties of Polyvinyl Alcohol / Methyl Red Composite Irradiated by Violet Laser

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ABSTRACT

The present work investigates optical parameters of Polyvinyl alcohol / Methyl red (PVA/MR) thick films. The work aims to enhance the optical properties of a PVA/MR composite by laser irradiation. The composite has been deposited on a petri dish by casting method with 9000 nm thickness. The PVA/MR thick films were irradiated by a violet laser with wavelength is 405 nm. and 20 mW power for different irradiation intervals (0, 20, 30 and 40) minutes. The optical properties were investigated in the spectral range (190-1100) nm as a function of the irradiating time. The absorption coefficient and the optical bandgap (E_g) increased while refractive index (n) and extinction coefficient (k_{ex}) values, dielectric constants (ε_i , ε_r) and the optical conductivity decreased with increasing the laser exposure time.

1. INTRODUCTION

Polyvinyl alcohol (PVA) is a linear, semicrystalline compound composed of a hydroxyl (OH) functional group and a carbon chain serving as the backbone [1]. This polymer is produced through the polyvinyl acetate (PVAC) hydrolysis, and the degree of hydrolysis has a major impact on the material's physical properties. PVA has a broad molecular weight range of 9000–186,000 g/mol [2]. As a result, it is considered a versatile polymer [3]. PVA is a very well hydrophilic and water-soluble polymer. Other advantageous characteristics of PVA include its accessibility., non-toxic, Biodegradability, minimal cost, and exceptional film formation, and biocompatibility, good chemical resistance, The PVA is an appealing choice for a variety of applications, including the formation of coatings, hydrogels, fibers, scaffolds, composites, and polymers, due to its thermal resistance and adhesion films [4]. PVA is given by the formula (C_2H_4O) and chemicallyPVA is classified as a homopolymer of vinyl alcohol or ethanol. Figure 1 illustrates the structural formula of PVA [5].

Methyl red is classified as an organic compound due to the carbon and hydrogen in the atomic structure, supplemented by nitrogen and oxygen elements. In the study of organic chemistry, these structural elements are commonly known as functional groups. Two rings within the molecule contain double bonds; these rings are referred to as aromatic or benzene rings [6].

The main application of the MR serves as an indicator of the benzenoid structure (yellow) in a base medium and the quinonoid structure (red) in acidic medium. As a pH indicator, methyl red can be applied to radiochromic material [7]. The chemical formula of the Methyl red is $C_{15}H_{15}N_3O_2$ as illustrated in Figure 2.

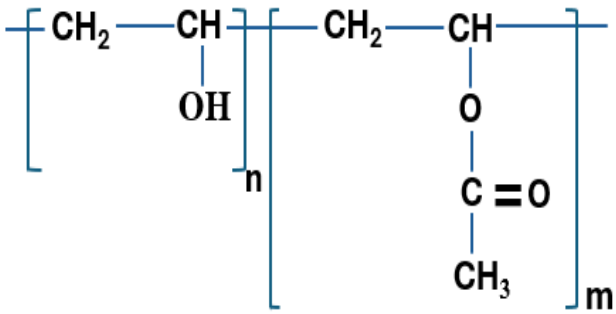

Figure 1. Structure of PVA [8]

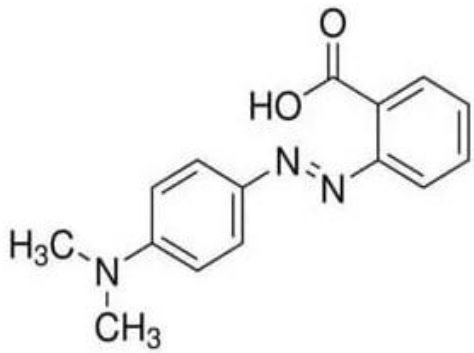

Figure 2. Methyl red dye's structure [9]

Two or more substances are combined to form a composite material, with the finished assembly possessing attributes superior to the individual parts [10]. The laser radiation is transmitted and reflected when it strikes a surface (the air-solid contact). Some of the beams are reflected, some are absorbed, and some are transmitted. According to Beer Lambert's law, it is absorbed when it moves across a new medium [11]:

$$I = I_0 e^{-\alpha t} \quad (1)$$

where, I_o and I are the intensity of the transmitted and incident photons respectively,

(α) represents the absorption coefficient, while (t) represents the sample's thickness.

Examining the optical properties of this combined material has an important impact across various fields for instance pH sensing for food packaging [12].

designing optoelectronic devices [13], manufacturing the biological sensors to detect pollutants and toxins [12] besides crucial research to understand the light-matter interaction [14, 15].

The optical characteristics present an information regarding the interaction between light and materials. The energy gap is equivalent to or smaller than the photon energy.

The electron-hole pair is composed of the maximum wavelength of the incoming photon λ, which is defined as [14]:

$$\lambda(nm) = \frac{hc}{E_g} = \frac{1240}{E_g(eV)} \quad (2)$$

The absorbance spectrum will be used in calculating the absorption coefficient of the films [16]:

$$\alpha = 2.303 \frac{A}{t} \quad (3)$$

The absorbance is denoted by A.

The extinction coefficient is calculated by [17]:

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

The ratio of the speed of light in a substance to the speed of light in a vacuum represents the refractive index. It may also be computed utilizing the following formula [18]:

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

For the calculation of reflectance, the following empirical relationship is used [19]:

$$R = 1 - \sqrt{T\, e \times p(A)} \quad (6)$$

where, T is the transmittance.

The real (ε_r) and imaginary (ε_i) part of the dielectric constants were obtained using the equations [20]:

$$\varepsilon_r = n^2 - k^2 \quad (7)$$

$$\varepsilon_i = 2nk \quad (8)$$

The materials' band gap is obtained from Tauc's equation of the following form [21]:

$$\alpha h\nu = B(h\nu - E_g)^r \quad (9)$$

The B constant is correlated with the structure of the sample and r represents the empirical index that signifies the electronic transition.

The optical conductivity of a material are given by the following relation [22]:

$$\sigma_{op} = \alpha n c \varepsilon_\circ = \frac{\alpha n c}{4\pi} \quad (10)$$

where, the velocity of light is denoted by c and $\varepsilon_\circ$ is the electrical permittivity of the space (8.854×10^{-12}F/m).

2. MATERIALS AND METHODS

Methyl red and polyvinyl alcohol powder were supplied by Sigma-Aldrich Company. In 20 ml of distilled water, 10,000 g/mol molecular weight, precisely 0.008 milligrams of PVA and 0.012 mg of MR with molecular weight (269.3 g/mol) are weighed and diluted at 90°C separately. The mixtures were subsequently vigorously stirred with a magnetic stirrer for approximately 10 minutes at room temperature, or until the PVA and MR had completely dissolved. Films were obtained by pouring the prepared polymer solutions and methyl red into petri dishes with the same diameter (2.5 cm) and then let them dry under identical atmospheric conditions. The films have a thickness of approximately 3 μm for PVA and 6 μm for MR, as determined by weight method. The same steps are repeated to obtain the (PVA/MR) composite with a thickness of about 9 μm under similar conditions. PVA and MR materials were chosen due to their compatibility in aqueous solutions which assists the MR dispersion in PVA matrix evenly. In addition, the PVA offers a stable and flexible substrate which suitable for applications that require bending and stretching. PVA/MR can response to the wavelengths (UV or visible) that makes it suitable for optical properties tuning.

The thick films are irradiated using a laser with a 405 nanometer wavelength (Violet) and a laser intensity of 20 mW for various applications time intervals (0, 20, 30 and 40) minute. Using the UV–Visible spectrophotometer (Shimadzu, UV-1900 I, JAPAN), the optical properties were measured before and after laser irradiation. An investigation is conducted on absorbance and transmittance spectra within (190 nm to 1100 nm) wavelength range. A local Excel program was used for calculations.

3. RESULTS AND DISCUSSION

The crystallite structure was determined using XRD (X-Ray Diffraction) characterization. The purified PVA thick films exhibited significant crystalline reflections at approximately 2θ = 19.92° and 42.74° in their X-ray diffraction pattern. Characteristic of PVA, the two peaks represent reflections from a monoclinic unit cell at (200) and (110). The results of the XRD data obtained for MR with a value of 2θ =12.745˚, 16.720˚, 24.773˚, 31.005˚and 44.949˚ there are five most substantial intensities, the highest peak at 12.745˚, Obtaining Miller's index from the intensity mentioned above, namely, (-101), (200), (211), (-122), and (311) which can show crystal

structure, as shown in Figure 3 (a) and (b).

Optical properties of PVA, MR and PVA/MR composite thick film measured before and after laser exposure with different irradiating times (0, 20, 30, and 40) minutes.

Figures 4-6 show the transmittance spectrum in the rang (275_460) nm for PVA, MR, and PVA/MR. It is clear that the transmittance spectra decreased with increasing irradiating time, which attributed to increasing the number of collisions between the incident photons and atoms.

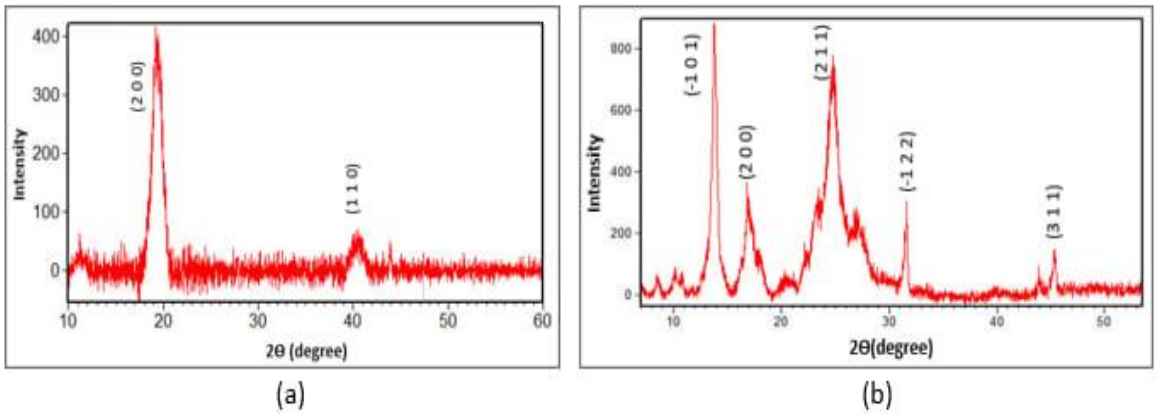

Figure 3. (a) Polyvinyl alcohol and (b) Methyl red X-ray diffraction patterns

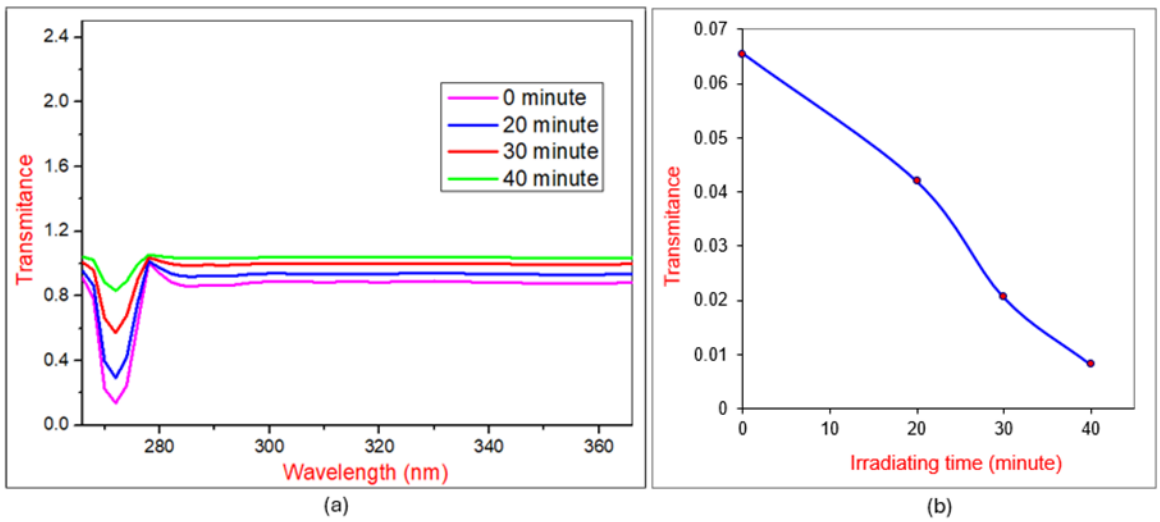

Figure 4. (a) The PVA thick films transmittance spectra of 3 μm thickness for different irradiating times (0, 20, 30 and 40) min. (b)The transmittance vs. irradiating times at 292 nm wavelength

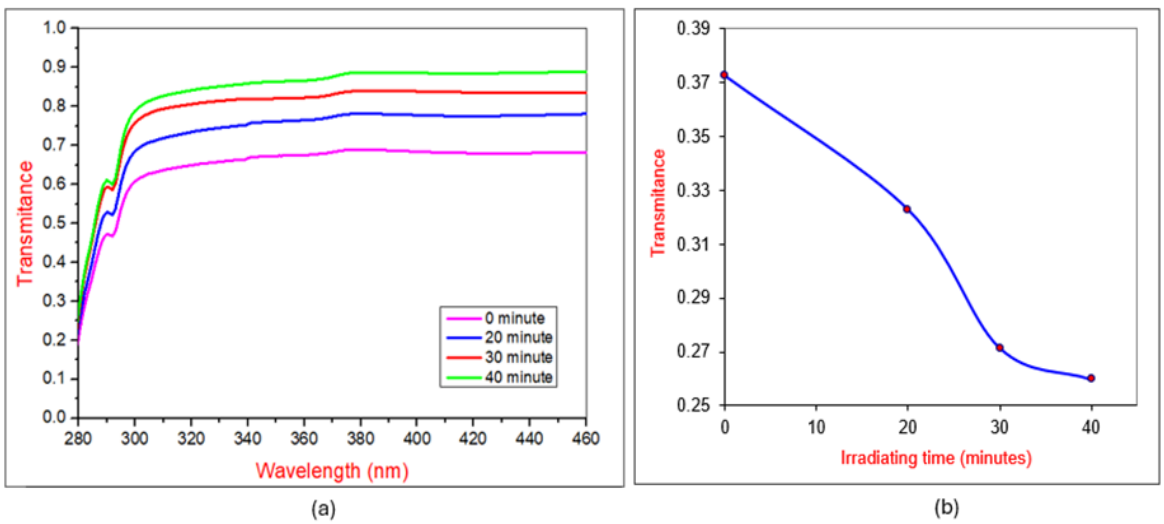

Figure 5. (a) The MR thick films transmittance spectra of 6 μm thickness for different irradiating times (0,20, 30 and 40) min. (b)The transmittance vs. irradiating times at 300 nm wavelength

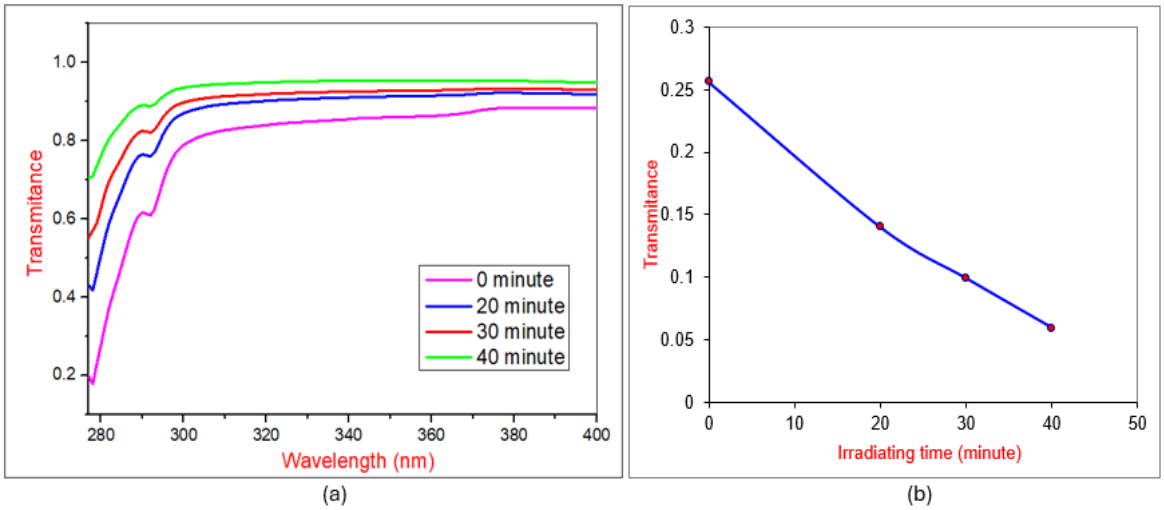

Figure 6. (a) The transmittance spectra of PVA/MR thick films of 9 μm thickness for different irradiating times (0,20, 30 and 40) min. (b) The transmittance vs. irradiating time at 300 nm wavelength

Figures 7-9 the reflectance spectrum (R) of a PVA and MR and (PVA/MR) composite thick film before and after green laser irradiating. The reflectance decreases with the increasing the wavelength but increases with increasing the exposure time. The high peak is observed at a PVA wavelength of 280 nm. The spectrum of 6 μm thickness of MR and PVA/MR thick films of 9 μm thickness is at 300 nm.

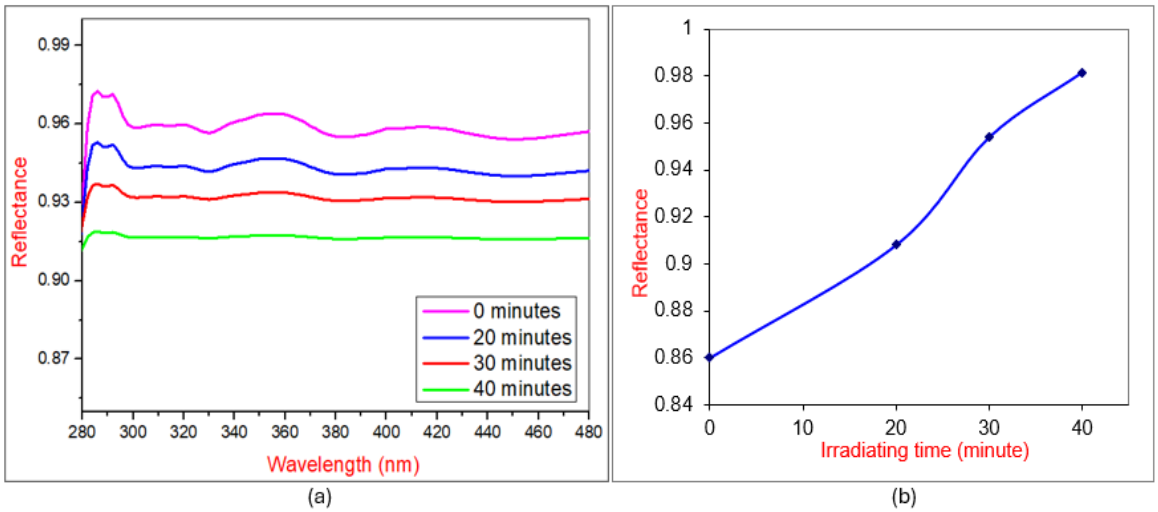

Figure 7. (a) Reflectance spectra of PVA. (b) Maximum reflectance vs. laser irradiation time at 300nm wavelength

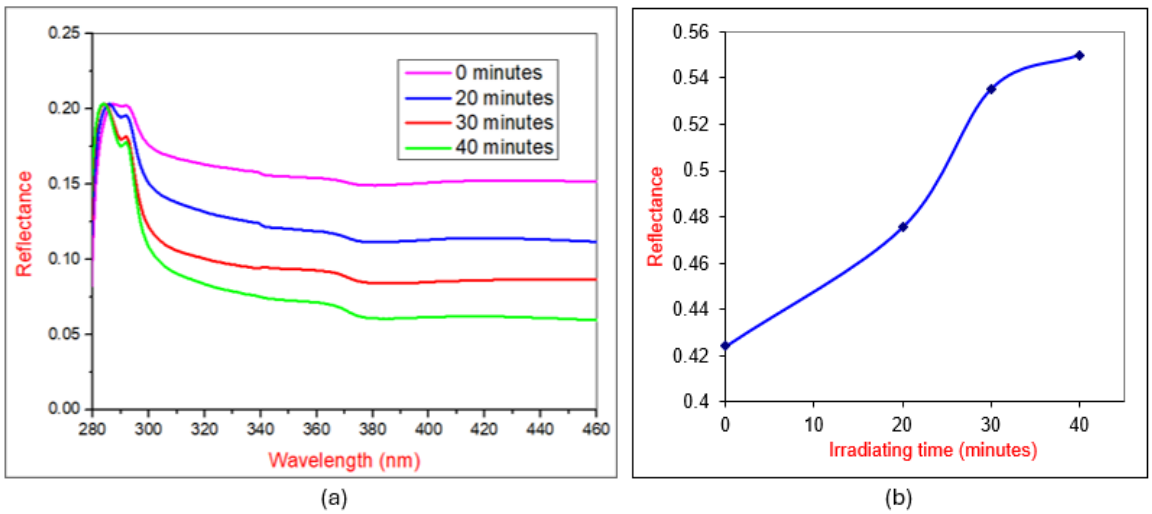

Figure 8. (a) Reflectance spectra of MR. (b) Maximum reflectance vs. laser irradiation times at 300nm wavelength

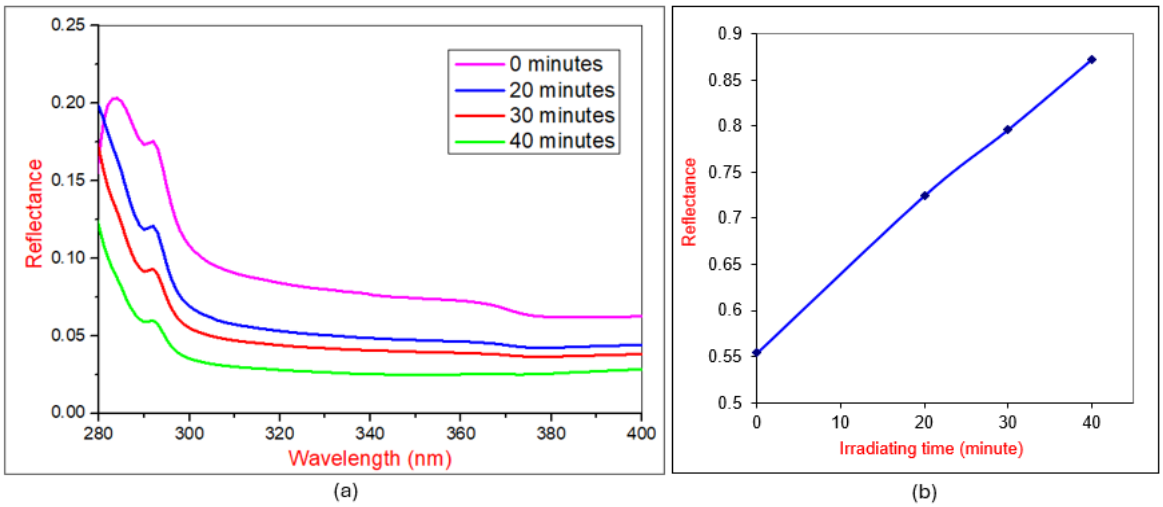

Figure 9. (a) Reflectance spectra of PVA/ MR Composite. (b) Maximum reflectance vs. laser irradiation times at 300nm wavelength

Figures 10-12 show the energy gap that is determined by extrapolating the linear part of $(\alpha hv)^{1/2}$ towards the (hv) axis leading to an estimated value that listed in Tables 1-3. Increasing the band gap with increasing the irradiation time as a result of decreasing the absorption leading to the decrease in the secondary levels between the bands.

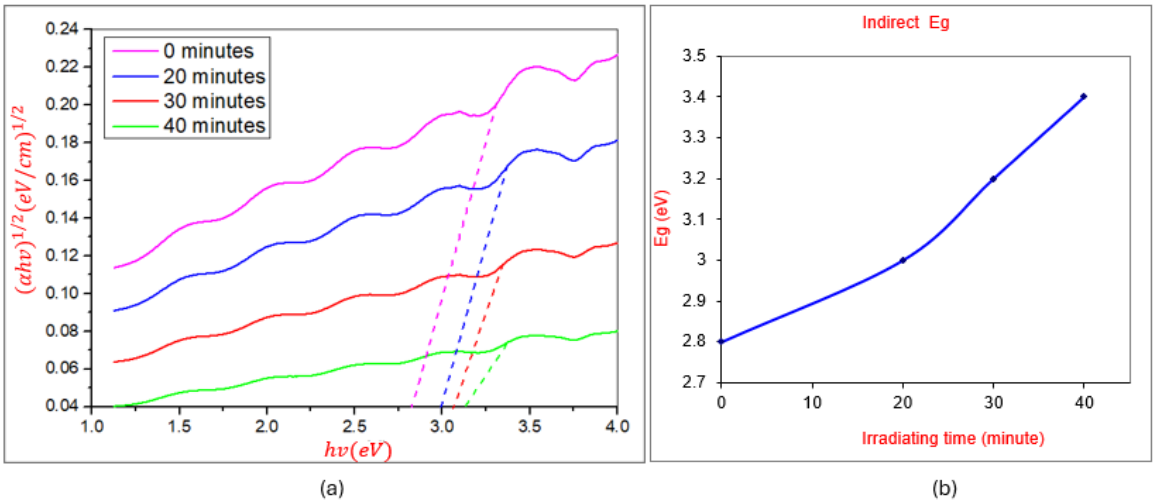

Figure 10. (a) The $(\alpha hv)^{1/2}$ of PVA vs. the photon energy of 3 μm thickness for different irradiating times (0, 20, 30 and 40) minutes. (b)The indirect band gap vs. irradiating times at 292 nm

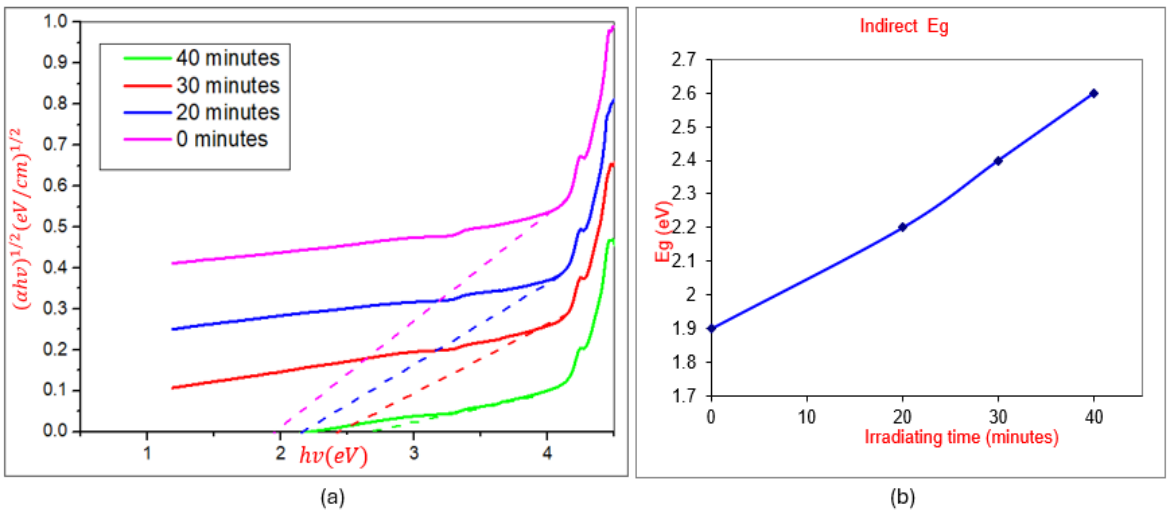

Figure 11. (a) The $(\alpha hv)^{1/2}$ of MR vs. the photon energy of 6 μm thickness for different irradiating times (0, 20, 30 and 40) minutes. (b)The indirect band gap vs. irradiating times at 300 nm

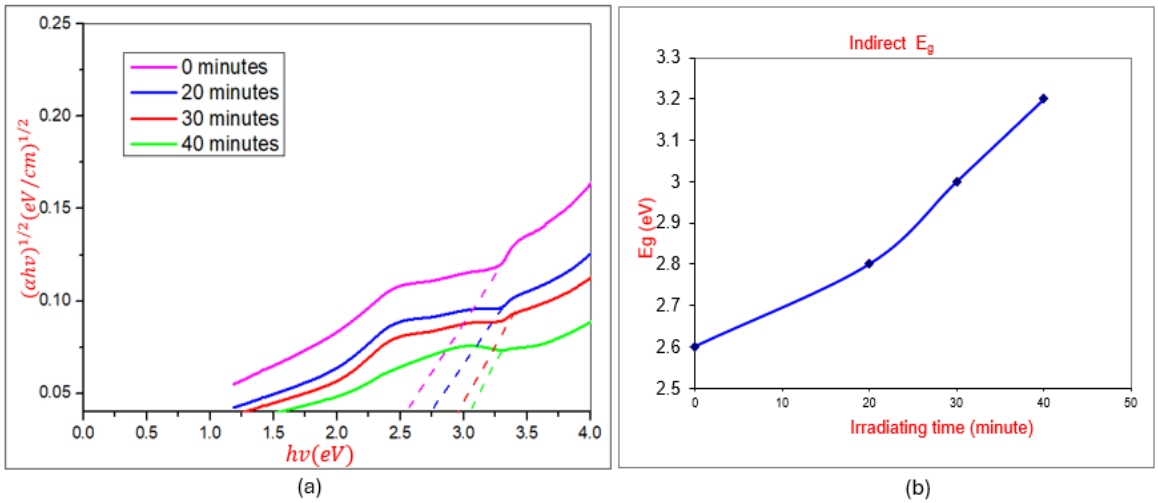

Figure 12. (a) The $(\alpha hv)^{1/2}$ of PVA/MR of 9 μm thickness vs. the photon energy for different irradiating times (0,20, 30 and 40) minutes. (b) The indirect band gap vs. irradiating times at 300 nm

Figure 13-15 illustrate the variation of optical conductivity, σ_opt in relation to the wavelength. the optical conductivity for (0, 20, 30 and 40) minutes for a polymer with a thickness 3 µm decreases exponentially with increasing of the wavelength noticing that it is moving toward the lower wavelength by increasing time.

The optical absorption coefficient of PVA, MR, and PVA/MR The significance of films is that it offers insight into the energy gap, band tail, and electronic band structure.

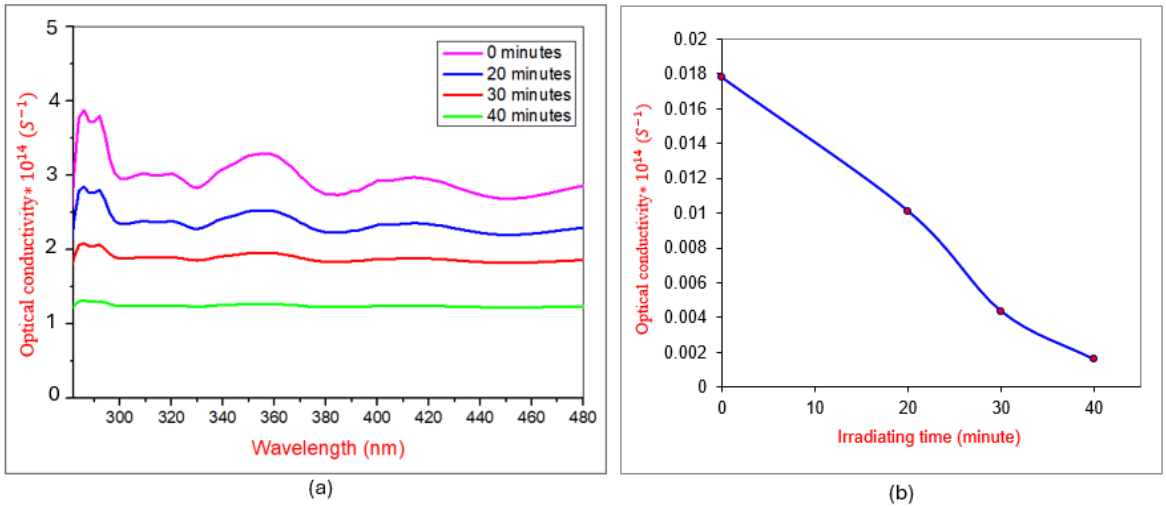

Figure 13. The correlation between polyvinyl alcohol's optical conductivity and wavelength

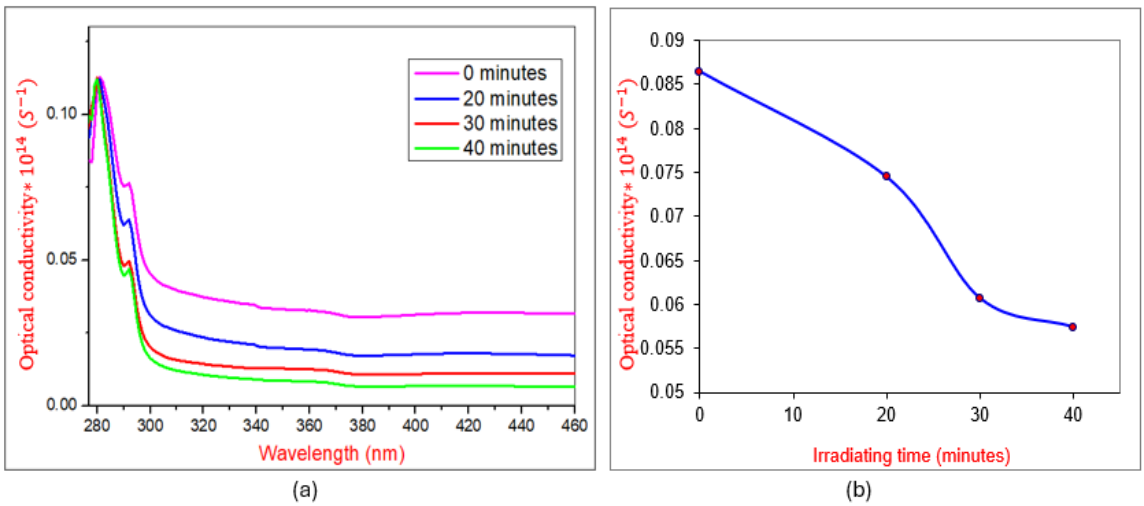

Figure 14. The correlation between methyl red optical conductivity and wavelength

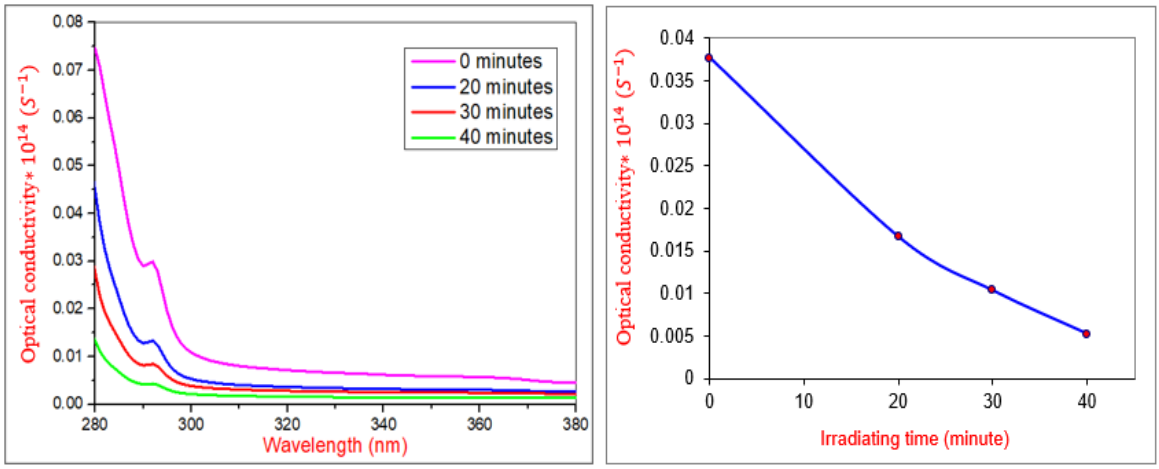

Figure 15. The optical conductivity as a function of the wavelength of PVA /MR

Table 1. The optical parameters of PVA composite at a wavelength of 290 nm

Irradiating Time (min)	$\alpha * 10^{14}\ (cm^{-1})$	k	n	ε_{real}	ε_i	$E_g\ (eV)$	$\sigma_{op}(s^{-1})$
0	0.050	0.0011	1.48	2.19	0.032	2.972	0.0176
20	0.032	0.0007	1.31	1.73	0.0019	3.015	0.010
30	0.015	0.0003	1.15	1.34	0.0008	3.05	0.004
40	0.006	0.0001	1.06	1.13	0.0003	3.11	0.0015

Table 2. The optical parameters of MR composite at a wavelength of 300 nm

Irradiating Time (min)	$\alpha * 10^{14}\ (cm^{-1})$	k	n	ε_{real}	ε_i	$E_g\ (eV)$	$\sigma_{op}(s^{-1})$
0	0.142	0.0032	2.53	6.40	0.016	2.97	0.086
20	0.123	0.0028	2.51	6.32	0.0014	3.01	0.074
30	0.104	0.0023	2.43	5.94	0.0011	3.05	0.060
40	0.099	0.0022	2.41	5.81	0.010	3.11	0.057

Table 3. The optical parameters of PVA/MR composite at a wavelength of 300 nm

Irradiating Time (min)	$\alpha * 10^{14}$ $(cm)^{-1}$	k	n	ε_{real}	ε_i	$E_g(eV)$	$\sigma_{op\ (s^{-1})}$
0	0.065	0.0014	2.40	5.77	0.0071	2	0.037
20	0.035	0.0008	1.94	3.76	0.0031	2.1	0.016
30	0.025	0.0005	1.70	2.90	0.0019	2.3	0.010
40	0.015	0.0003	1.44	2.07	0.0010	2.5	0.005

4. CONCLUSION

Absorbance spectra were recorded for PVA, MR and PVA/MR composite to be able to calculate the optical parameters as a response of the laser effect. It was found that $k, n, \varepsilon_r, \varepsilon_i$, and σ_{opt} decreased while E_g increased by the increase of the irradiating time. the irradiation time presents a great opportunity for bonds breakage, thus decreases the thick films absorption, and then increase in the energy gap E_g. This has a suitable application in manufacturing the optical filters. Although, the laser irradiation can improve the films' structure, controlling the energy gap and the optical parameters. The casting method is a fast and easy deposition method, but there are some experimental limitations have to be avoided in the next research such us the humidity sensitivity and temperature. In addition, the films processing method determines the composite homogeneity which affect some industrial applications.

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