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Effect of Laser Irradiation with 532 nm Wavelength on The Optical Properties of PVA/MR Solutions

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تأثير إشعاع الليزر ذو الطول الموجي 532نانومتر على الخواص البصرية لمحاليل بولي فينيل الكحول والمثيل الأحمر

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ABSTRACT

Background: This work aims to study the impact of 532 nm laser irradiating on the optical properties of the Polyvinyl alcohol/ Methyl Red (PVA/MR) solution before and after laser irradiation 32mW with various times (0, 20, 30 and 40) minutes.

Materials and Methods:
The polymer (PVA) powder 500 mg was dissolved in 50 ml distilled water at temperature 80 ˚C and the methyl red (MR) 30 mg was dissolved in 10 ml at temperature 80 ˚C using solution dilution formula $C_1V_1 = C_2V_2$. A semiconductor laser with a wavelength of 532 nanometers was used to irradiate the solution.

Results:
The absorbance, reflectance, and transmittance spectrum of solution prior to and following laser irradiation were recorded. Then, the optical constants and energy gap were calculated.

Conclusions:
The irradiation with the 532nm laser leads to a break of the bonds (From the absorbance spectrum, it decreases as the irradiation time increases. This indicates the breaking of bonds.) that results in an increase in the transmittance spectrum, and the energy gap.

Key words: PVA/MR; Optical properties; green laser irradiation; indirect energy gap.

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INTRODUCTION

Polymers have numerous benefits, including low cost, flexibility, high strength, and excellent mechanical properties. Material suitability for optoelectronic and photonic applications can be achieved with polymers [1]. A linear or semi-crystalline synthetic polymer, polyvinyl alcohol is granular or pulverized, whitish, odorless, tasteless, innocuous, biocompatible, and thermostable [2]. Application fields, such as biomedical, sensors, and computation, have noticed a surge in its significance [3]. The PVA chemical structural is illustrated in Figure 1.

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 [4]. 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 [5]. The chemical formula of the Methyl Red is $C_{15}H_{15}N_3O_2$ as illustrated in Figure 2.

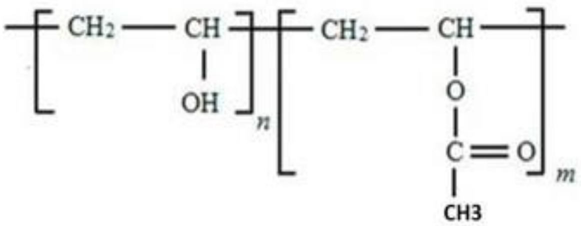

Fig. 1: Structure of PVA [6]

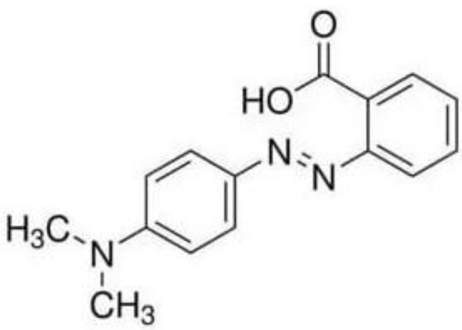

Fig. 2: Methyl Red dye's structure [7].

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[8]**:**

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

Where I_o and I are the intensity of the incident and transmitted photons respectively, (α) is the absorption coefficient and (t) is the thickness of sample.

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

The electron-hole pair is composed of the photon's maximal wavelength, denoted as λ, which is defined as [9]**:**

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

The absorbance spectrum is used in calculating the absorption coefficient of the films: [10]:

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

Where A is the absorbance, from which the extinction coefficient (k) is calculated [11]:

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

The ratio of the speed of light in a substance to the speed of light in a vacuum results the refractive index (n). It may also be computed utilizing the subsequent formula [12]:

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

For the calculation of reflectance, the following relationship is used [13]:

$$R = 1 - \sqrt{T\,exp(A)} \qquad (6)$$

Where T is the transmittance.

The real (ε_r) and imaginary (ε_i) part of the dielectric constant were obtained using the equations [14]:

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

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

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The materials' band gap energy is derived from Tauc equation of the following form [9]:

$$\alpha hv = B(hv - E_g)^r \qquad (9)$$

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 [15]:

$$\sigma_{op} = \alpha nc\varepsilon_{\circ} = \frac{\alpha nc}{4\pi} \qquad (10)$$

Where c is the velocity of light and $\varepsilon_{\circ}$: equal to ($8.854x10^{-12}$F/m) the electrical permittivity of the space.

MATERIALS AND METHODS

The polyvinyl alcohol and Methyl Red powder were supplied by Sigma-Aldrich Company, Where it is dissolved in 50 ml of distilled water, precisely 500 mg of PVA and 30 mg of MR in 30 ml of water are weighed and diluted at 80 ˚C. 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. The solution are irradiated using a laser with a 532 nanometers wavelength (Green) and 32 mW laser power for various time intervals (0, 20, 30 and 40) minute. Using the UV–Vis spectrophotometer (Shimadzu, UV-1900 I, JAPAN), the optical properties were obtained before and after laser irradiation. An investigation is conducted on the absorbance spectra and transmittance within the wavelength range of (190−1100) nm. The crystal structure of PVA and MR was investigated by XRD.

RESULTS AND DISCUSSION

The purified PVA thick films exhibited significant crystalline reflections at approximately 2θ = 19.92° and 42.74° in their X-ray diffraction (XRD) pattern. The two peaks in the PVA X-ray pattern represent reflections from a monoclinic unit cell at (200) and (110).**[since the sample is solution so we can’t perform XRD]**

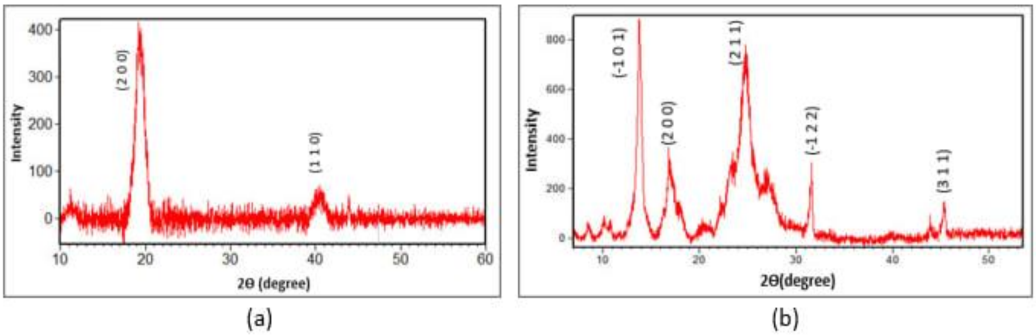

Fig. 3: (a) Polyvinyl alcohol and (b) Methyl Red X-ray diffraction patterns.

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The UV-Visible absorption spectrum of purified PVA/MR solution is measured both prior to and after irradiation for durations of 0, 20, 30, and 40 minutes. the absorbance spectrum in the rang (330_610) nm for PVA,MR, and PVA/MR At 460 nm, the PVA/MR solution exhibits an absorption peak in the ultraviolet region. The absence of absorption peaks is noted at longer wavelengths. The absorbance peaks shift red to the visible wavelengths as a result of laser irradiation. In addition, as the irradiation times increase, the absorption decreases due to the break of intermolecular bonds, illustrated in Figure 2.

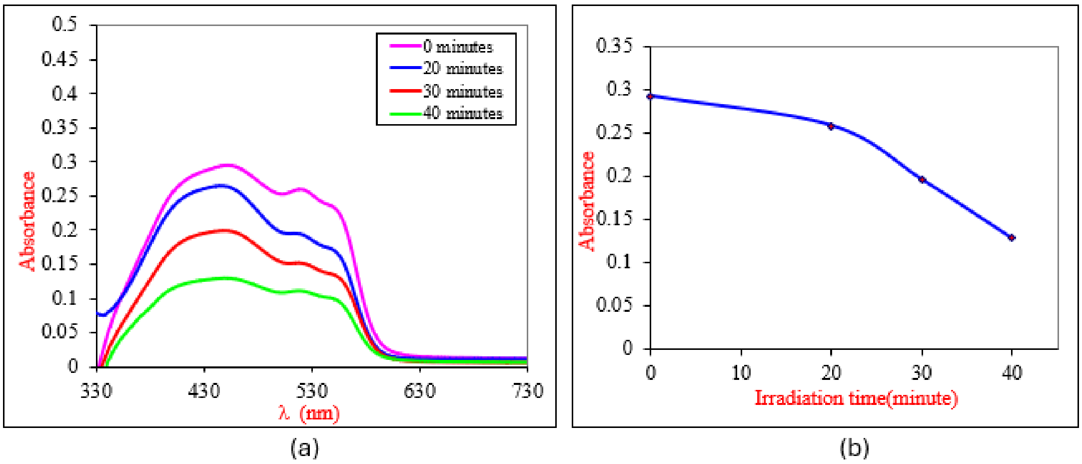

Fig. 4:(a) The absorbance spectrum of PVA /MR solution for different irradiating times (0, 20, 30 and 40) min. (b)The absorbance vs. irradiating times at 460 nm wavelength.

Figure 5 shows the transmittance as a function of the wavelength. Transmittance decreases as the irradiation time increases, this phenomenon can be ascribed to the escalating quantity of collisions that occur between incident photons and film atoms.

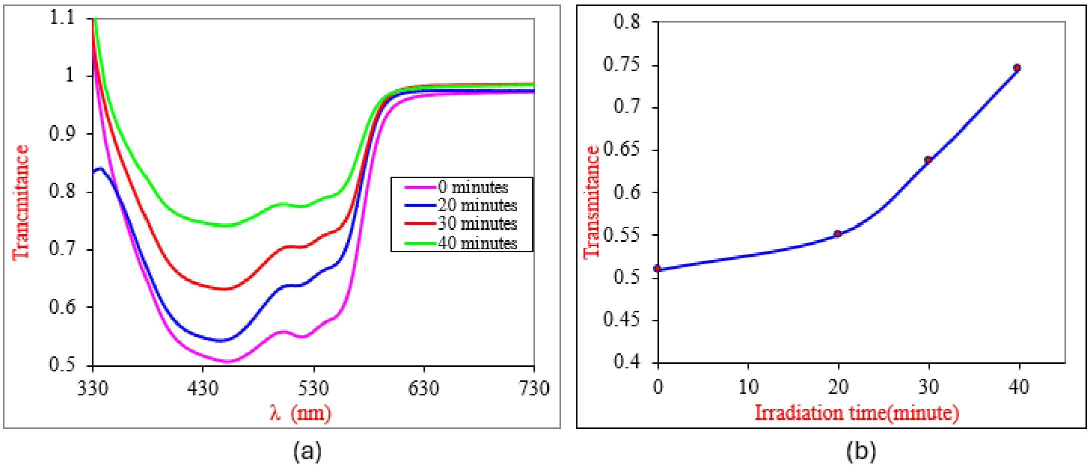

Fig. 5:(a) The PVA/MR solution transmittance spectra for different irradiating times (0, 20, 30 and 40) min. (b)The transmittance vs. irradiating times at 460 nm wavelength.

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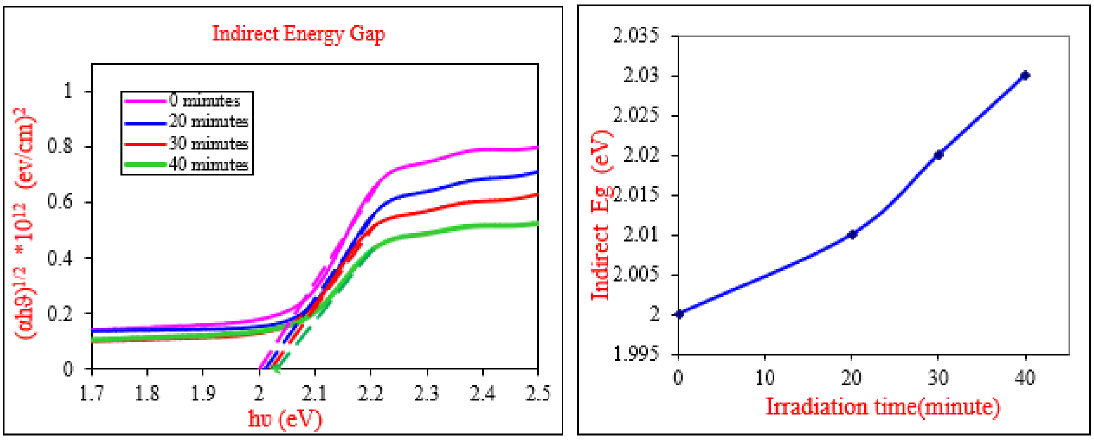
Figure 6 shows the band gap for allowed indirect transitions (r =1/2). The energy gap is determined by extrapolating the linear part of $(\alpha h\nu)^{1/2}$ towards the $(h\nu)$ axis leading to an estimated value that listed in Tables 3. It is found that the band gap increases with increasing the irradiation time as a result of decreasing the absorption. The result is In agreement with [16][9].



(a) (b)

Fig.6: (a) The $(\alpha h\nu)^{1/2}$ of PVA/MR solution vs. of the photon energy for different irradiating times (0,20, 30 and 40) minutes. (b) The indirect band gap vs. irradiating times at 300 nm.

Table1: The optical parameters of PVA/MR composite at a wavelength of 300 nm.

Irradiating time(minute)	$\alpha * 10^{14}$ (cm^{-1})	k	n	ε_{real}	ε_i	E_g (eV)	$\sigma_{op}(s^{-1})$
0	0.292	0.00133	2.477	6.136	5.306	2	0.173
20	0.258	0.00096	2.404	5.783	4.550	2.01	0.148
30	0.196	0.00085	2.205	4.863	3.169	2.02	0.103
40	0.128	0.00082	1.876	3.520	1.762	2.03	0.057

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CONCLUSION

Absorbance spectra were recorded for PVA/MR solution to be able to calculate the optical parameters as a response of the laser effect. It was found that , K, n, ε_r, ε_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. It is concluded that the laser irradiation can improve the films' structure, control the energy gap and the optical parameter. Examining the optical properties of this combined material has an important impact across various fields for instance pH sensing for food packaging. designing optoelectronic devices, manufacturing the biological sensors to detect pollutants and toxins, besides crucial research to understand the light-matter interaction.

Conflict of interests

There are non-conflicts of interest

References

[1] Z. Ali Abdulrassol, A. Qassim Abdullah, and S. Sh. Al-Lauiby, "Structural and Optical Properties of New Poly vinyl Alcohol Grafted Methyl Red (PVA-g-MR)," *J. Kufa-Physics*, vol. 9, no. 2, pp. 1–10, 2017, doi: 10.31257/2018/jkp/2017/v9.i2.9415.

[2] I. Saini, A. Sharma, R. Dhiman, S. Aggarwal, S. Ram, and P. K. Sharma, "Grafted SiC nanocrystals: For enhanced optical, electrical and mechanical properties of polyvinyl alcohol," *J. Alloys Compd.*, vol. 714, pp. 172–180, 2017.

[3] S. Tang, Y. Zeng, and X. Wang, "Splashing needleless electrospinning of nanofibers," *Polym. Eng. Sci.*, vol. 50, no. 11, pp. 2252–2257, 2010.

[4] D. K. Das, P. Goswami, C. Barman, and B. Das, "Methyl red: a fluorescent sensor for Hg 2+ over Na+, K+, Ca 2+, Mg 2+, Zn 2+, and Cd 2+," *Environ. Eng. Res.*, vol. 17, no. S1, pp. 75–78, 2012.

[5] W. Chairunisa and C. Imawan, "The effect of pH on the characteristics of the methyl red solution as a gamma-ray dosimeter," in *Journal of Physics: Conference Series*, IOP Publishing, 2019, p. 22015.

[6] T. S. Gaaz, A. B. Sulong, M. N. Akhtar, A. A. H. Kadhum, A. B. Mohamad, and A. A. Al-Amiery, "Properties and applications of polyvinyl alcohol, halloysite nanotubes and their nanocomposites," *Molecules*, vol. 20, no. 12, pp. 22833–22847, 2015.

[7] J. B. Benedict, D. E. Cohen, S. Lovell, A. L. Rohl, and B. Kahr, "What is syncrystallization? States of the pH indicator methyl red in crystals of phthalic acid," *J. Am. Chem. Soc.*, vol. 128, no. 16, pp. 5548–5559, 2006.

[8] Y.-C. Yeh, B. Haasdonk, U. Schmid-Staiger, M. Stier, and G. E. M. Tovar, "A novel model extended from the Bouguer-Lambert-Beer law can describe the non-linear absorbance of potassium dichromate solutions and microalgae suspensions," *Front. Bioeng. Biotechnol.*, vol. 11, p. 1116735, 2023.

ISSN: 2312-8135 | Print ISSN: 1992-0652

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[9] S. M. Tareq, N. A. Abdulwahhab, and A. H. Al-araji, “Effect of Violet Laser Irradiation on the Optical Properties of Polyvinyl Alcohol / Methyl Orange Composite Thick Films : A Model for Medical Applications". Eng. Proc. 59, 236. https://doi.org/ 10.3390/engproc2023059236 Academic Academic,” pp. 1–9, 2024.

[10] N. A. AbdulWahhab, “Optical properties of SnO2 thin films prepared by pulsed laser deposition technique,” *J. Opt.*, vol. 49, no. 1, pp. 41–47, 2020.

[11] E. M. Nasir, M. T. Hussein, and A. H. Al-Aarajiy, “Investigation of Nickel Phthalocyanine Thin Films for Solar Cell Applications,” *Adv. Mater. Phys. Chem.*, vol. 9, no. 08, pp. 158–173, 2019.

[12] O. G. Abdullah and D. R. Saber, “Optical absorption of polyvinyl alcohol films doped with nickel chloride,” *Appl. Mech. Mater.*, vol. 110, pp. 177–182, 2012.

[13] E. M. Abdelfattah *et al.*, “Enhancement of the Structure, Thermal, Linear/Nonlinear Optical Properties, and Antibacterial Activity of Poly (vinyl alcohol)/Chitosan/ZnO Nanocomposites for Eco-Friendly Applications,” *Polymers (Basel).*, vol. 15, no. 21, 2023, doi: 10.3390/polym15214282.

[14] N. F. Habubi and S. S. Chiad, “Optical Properties of Doped Polymers,” *Diyala J. Pure Sci.*, vol. 7, no. June, pp. 153–161, 2017.

[15] H. R. Jappor, M. A. Habeeb, and A. Hashim, “The Effect of Sodium Fluoride on Optical Properties of Polyvinyl pyrrolidone,” *Chem. Mater. Res.*, vol. 3, pp. 956–962, 2013.

[16] S. M. T, N. A. AbdulWahhab, and A. H. Al-Araji, “Study the Optical Properties of Polyvinyl Alcohol Thick Film Irradiated with Violet Laser,” *J. Univ. BABYLON Pure Appl. Sci.*, vol. 31, no. 3, pp. 137–146, 2023, doi: 10.29196/jubpas.v31i3.4834.

الخلاصة

الخلفية: يهدف هذا العمل إلى دراسة تأثير التشعيع بالليزر 532 نانومتر على الخواص البصرية لمحلول كحول البوليفينيل/ أحمر الميثيل ((PVA/MR) قبل وبعد التشعيع بالليزر 32 ملي واط بأوقات مختلفة (0، 20، 30، 40) دقيقة..

المواد وطرائق العمل: تم إذابة مسحوق البوليمر 500 (PVA) ملغ في 50 مل من الماء المقطر عند درجة حرارة 80 درجة مئوية وتم إذابة الميثيل الأحمر 30 (MR) ملغ في 10 مل عند درجة حرارة 80 درجة مئوية باستخدام صيغة تخفيف المحلول =V_1 C_1 ج_2 ف_2. تم استخدام ليزر أشباه الموصلات بطول موجة 532 نانومتر لتشعيع المحلول.

النتائج: تم تسجيل طيف الامتصاص والانعكاس والنفاذية للمحلول قبل وبعد تشعيع الليزر. ثم تم حساب الثوابت الضوئية وفجوة الطاقة.

الاستنتاجات: يؤدي التشعيع بالليزر 532 نانومتر إلى كسر الروابط (من طيف الامتصاص، يتناقص مع زيادة وقت التشعيع. وهذا يشير إلى كسر الروابط.) مما يؤدي إلى زيادة في طيف النفاذية، وفجوة الطاقة.

الكلمات المفتاحية: الخصائص البصرية، تشعيع الليزر الأخضر، فجوة الطاقة غير المباشرة.

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