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Study the optical properties and FTIR spectroscopy of polyvinyl alcohol doped by potassium permanganate films

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A B S T R A C T

The casting method was used to prepared pure polyvinyl alcohol PVA and doped by potassium permanganate ($PVA/KMnO_4$) films, with different weight ratios (2, 4, 6, 8) Wt% of potassium permanganate in order to investigate the impact of potassium permanganate on the optical properties and FTIR spectroscopy of the prepared films. Infrared spectra in the wavenumber range (600-2000) cm^{-1} used to study the effect of doped on the functional groups of polyvinyl alcohol. UV-VIS spectroscopy was used to study the optical properties for the samples and based on these spectra, the optical energy gap was calculated, which was in the range 3.2 eV for the pure films and decreases with increasing the doping ratio of potassium permanganate to be 2.62 eV. The absorption coefficient, extinction coefficient, refractive index, the dielectric constant and optical conductivity were also studied under the influence of doping ratios.

Kyeword :- *Polyvinyl alcohol, potassium permanganate, casting method.*

1. Introduction

Since the dawn of history, ancient man has used polymeric plant and animal products for various purposes in his daily life, and only a century ago, the unique characteristics of polymers gathered in humans, and the name colloids was used at that time to denote polymeric materials at that time. The systematic scientific study of the polymerization mechanics and the nature of the forces acting between polymeric particles began after 1900, when the scientists Mark and Mayer were able to know the stereochemistry of rubber in the year 1928. Nylon was discovered in 1928, PVPD in 1937, polyethylene in 1937 and Teflon in 1938. The scientists Carl Zieglar and Giullio Natta were awarded the Nobel Prize for the first discovery of catalysts for the initiation of polymerization reactions and for the second development of these factors and their use in the polymer industry [1].

One goal of materials science research is to develop novel materials with qualities customized to a certain type of application, as well as to comprehend the physical and chemical mechanisms that govern these features. Polymers have opened up an enormous wave of research worldwide, due to their promising potential in applications of industrial such as optical devices, especially in the recent period, it has become widely used in touch screen applications and smart screens used in most modern display devices. As a device with a screen no longer dispenses with smart screens or touch screens. The most common polymeric materials in used are polyvinyl alcohol (PVA), polymethyl methacrylate (PMMA) and polyvinyl chloride (PVC) [2]. Many studies have been conducted to improve the properties of polymers by combining two or three polymers (polymer blends) or adding ingredients [4,3]. An alternate and simpler way is to change organic polymers by inserting material oxides, or by introducing material oxides into polymer side groups, where in general the characteristics of the polymer is improved and new properties different from both the matrix and the filler are obtained [4].

Studying the optical properties of pure and doped polymers with other material oxides by studying their absorption spectra are an extremely useful approach for understanding the fundamental mechanism of light interaction with pure or doped polymers, as well as providing details on the structure band and values of energy gap [5]. UV-vis absorption spectroscopy is a critical instrument for investigating the impact of changes or doped on the optical properties of the polymer [6]. A lot of attention has been committed to the optical characteristics of PVA films combined with many metal salts or material oxides [7], and easily notice in the literature a lot of studies on the optical properties of PVA combined with potassium permanganate $KMnO_4$, where potassium permanganate is an oxidizing inorganic chemical compound, characterized as widely available, cheap, easy to soluble in water, untoxic and safe [8]. Potassium permanganate is an environmentally friendly substance is used as disinfection for water in wide range, oxidation of toxic substances, in addition for killing algae in wastewater [9]. The goal objective of the current paper is to study the optical properties and infrared spectra of PVA films and the effect of potassium permanganate doping ratios on them. Where enough information about the optical energy gap, refractive index, etc. can be obtained from the optical parameters.

2. Experimental

The casting method was used to prepare pure and doped polyvinyl alcohol with potassium permanganate films. Polyvinyl alcohol with (Mw. 107 g/mol / BDH Co.) and potassium permanganate $KMnO_4$ from (BDH) was also used. To prepare a pure PVA solution, 0.1 g of granules from PVA were dissolved in 5 ml of distilled water and kept continuously stirring for 30 minutes at a temperature of approximately 70°C in order to obtain a homogeneous solution. Solutions enriched with potassium permanganate were prepared by dissolving PVA and permanganate in distilled water with weight ratios (2, 4, 6, 8) Wt%. These solutions were poured into Petri dishes and allowed to dry for two days at room temperature, using forceps were easily lifted. A digital micrometer was used to measure the thickness of the produced samples and was within about 20 µm. The characterization of the prepared films was carried out using a Shimadzu FTIR-8400S Fourier infrared spectrometer with a range of 600-2000 cm^{-1}. While the optical transmittance and absorption measurements were made using a Shimadzu Japan UV-160A spectrophotometer in the wavelength range 200-900 nm.

3 .Result and Discussion

The prepared samples in the paper were diagnosed using FT-IR spectrum to recognize the locations of the functional groups of the pure and doped samples. Figure (1) represents the infrared spectrum of pure polyvinyl alcohol films and PVA/$KMnO_4$ films at 8% Wt, where noticed the characteristic bands of pure polyvinyl alcohol films at wave numbers 1713, 1644, 1426, 1365, 1033 and 828 cm^{-1}, which refers to C=C stretching, C=O stretching, (C-H bending, C-H wagging, C-O-C stretching of acetyl groups and C-H rocking vibrations, respectively [4] [10].

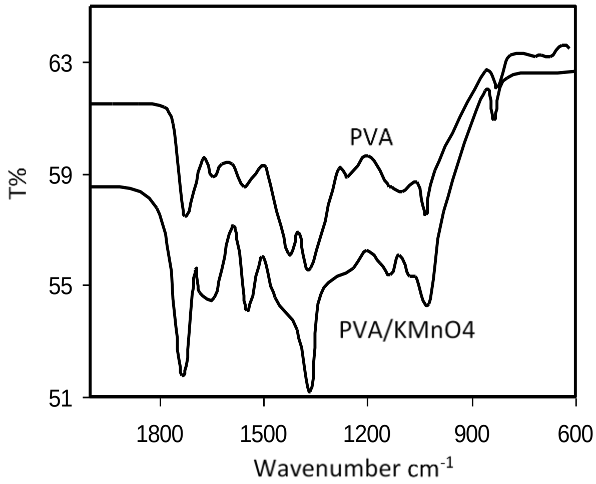

Figure (1). Infrared spectrum of pure polyvinyl alcohol and doped with potassium permanganate films.

From observing the infrared spectrum of the PVA/$KMnO_4$ films, noticed a slight shift in the locations of some peaks and the emergence of a new peak at the wave number 1547 cm^{-1} due to the presence of potassium permanganate, in addition to the increase in the intensity of these peaks, and this is a clear indication of the effect of $KMnO_4$ on the functional groups of polyvinyl alcohol [10] [11]. The values of absorbance and transmittance of the prepared films were measured. Figure (2) shows the absorption spectra of pure polyvinyl alcohol films and the doped with different weight ratios of potassium permanganate within the wavelength range 190-1000 nm, for the ultraviolet and visible spectral region, including that noted that the highest value of absorbance appears at length wavelength 330nm and the reason for this is due to the occurrence of electronic transitions between the energy levels of the molecule, where these transitions need the energy of ultraviolet photons, and the potential transition is $n \rightarrow \pi^*$, where this transition occurs at the region located above 200nm [12]. Also noted that the absorbance decreases with increasing wavelength. On the other hand, noticed an increase in the absorbance with increasing the weight ratios of potassium permanganate in the polymer matrix. This is due to the high absorbance of potassium permanganate.

Figure (3) shows the transmittance spectra of pure and doped polyvinyl alcohol films, from which noticed an increase in the transmittance values with wavelength, on the one hand, a decrease in transmittance with an increase in the weight ratios of potassium permanganate. Since it is known that the behavior of permeability is opposite to the behavior of absorption.

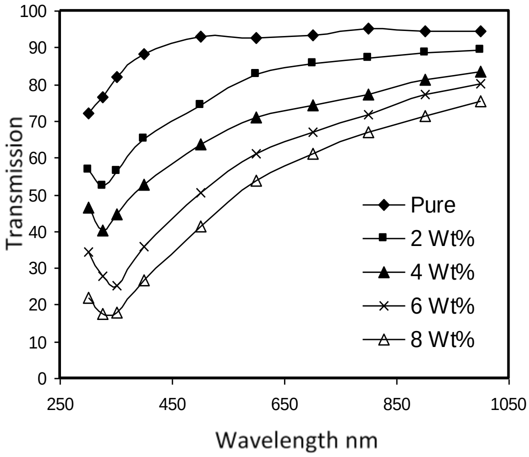

Figure (3). Transmittance spectrum of pure polyvinyl alcohol and doped with potassium permanganate films.

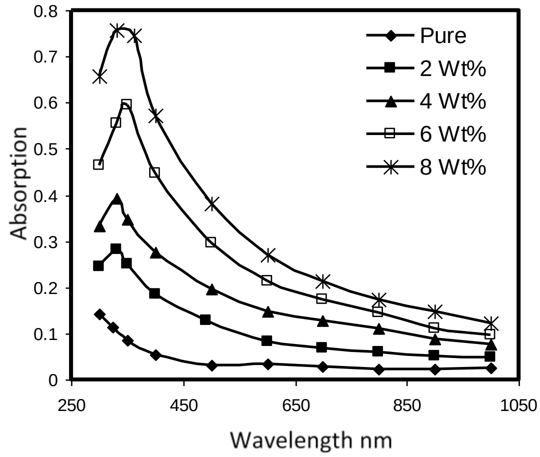

Figure (2). Absorption spectrum of pure polyvinyl alcohol and doped with potassium permanganate films.

The absorption coefficient α it was very important parameter and it is computed by used this equation [13]:-

$$\alpha = 2.303\,\frac{A}{d} \qquad (1)$$

Where: A the absorbance, d the thickness of the film.

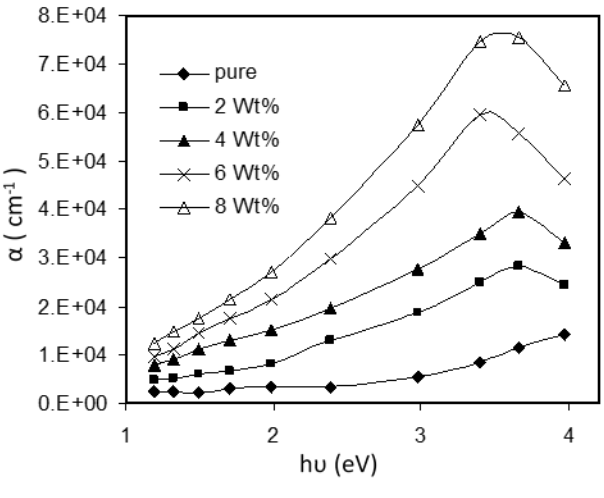

Figure (4). The relationship between the absorption coefficient and the energy of the incident photon for pure and doped polyvinyl alcohol films.

Figure 4. shows the relationship between the absorption coefficient as a function to the energy of the incoming photon for the pure and doped polyvinyl alcohol films, noted from the figure that the change in the α of prepared samples at low energies is relatively small, and therefore the probability of electronic transitions is low. In high energies, the absorption coefficient changes it is relatively large, and this indicates a high probability of electronic transitions, which is the absorption edge region.

Study the optical properties and FTIR

The α of prepared samples is useful in determining the nature of electronic transitions. Direct electronic transitions are expected to occur when the α of prepared samples values are large (10^4 cm^{-1} < α), in this case the electron and photon have conserved energy and momentum, however, when the α of prepared samples values are low (10^4 cm^{-1}>α), indirect electronic transitions are expected, which the electron and photon momentum with retained of the phonon [14]. The findings revealed that the values of the absorption coefficient for the films are greater than 10^4 cm^{-1}, which suggests direct electronic transmission. The forbidden energy gap was calculated in direct transmission of both types, allowed and forbidden, by depended on the equation [15]:

$$\alpha h\nu = A(h\nu - E_g)^m \qquad (2)$$

Where: hν the energy of the photon eV, A is the constant of proportionality, E_g the energy gap for forbidden direct transmission. If the value of m=1/2, the transmission is direct allowed. Figure (5) represents the relationship between $(\alpha h\nu)^2$ and the energy of the incoming photon for pure polyvinyl alcohol and doped films, and by taking the extension at $(\alpha h\nu)^2 = 0$, the straight part of the curve is used to cut the photon energy axis will get the value of the optical energy gap for the allowed direct transmission and note that the value of the energy gap decreases from about 3.2 eV for pure polyvinyl alcohol films to about 2.6 eV for doped with 8 Wt%, this is attributed to the fact that doping leads to the create of new energy levels between HOMO and LOMO and this leads to an increase in the density of local states in the energy gap of the doped PVA samples [10].

The extinction coefficient k, which represents the amount of energy absorbed by the thin layer. Figure (6) shows the k as a function of λ for pure and doped polyvinyl alcohol films, which was calculated from the relationship [16].

$$k = \frac{\alpha\lambda}{4\pi} \qquad (3)$$

From the figure, noticed a clear decrease in the k of samples with the increase in wavelength, especially at high wavelengths. On the other hand, due to the effect of increasing the doped pf potassium permanganate, noticed an increase in the extinction coefficient values with an increase in the doped rate. Whereas, an increase in the extinction coefficient indicates higher light scattering due to scattering and absorption by potassium permanganate molecules diffused in the polymeric matrix, and this is consistent with the results of Mott and Davis [19-17].

The refractive index of pure and doped polyvinyl alcohol films, which was calculated from equation [20]

$$n = \left[\frac{4R}{(R-1)^2} - k^2\right]^{1/2} - \frac{(R+1)}{(R-1)} \qquad (4)$$

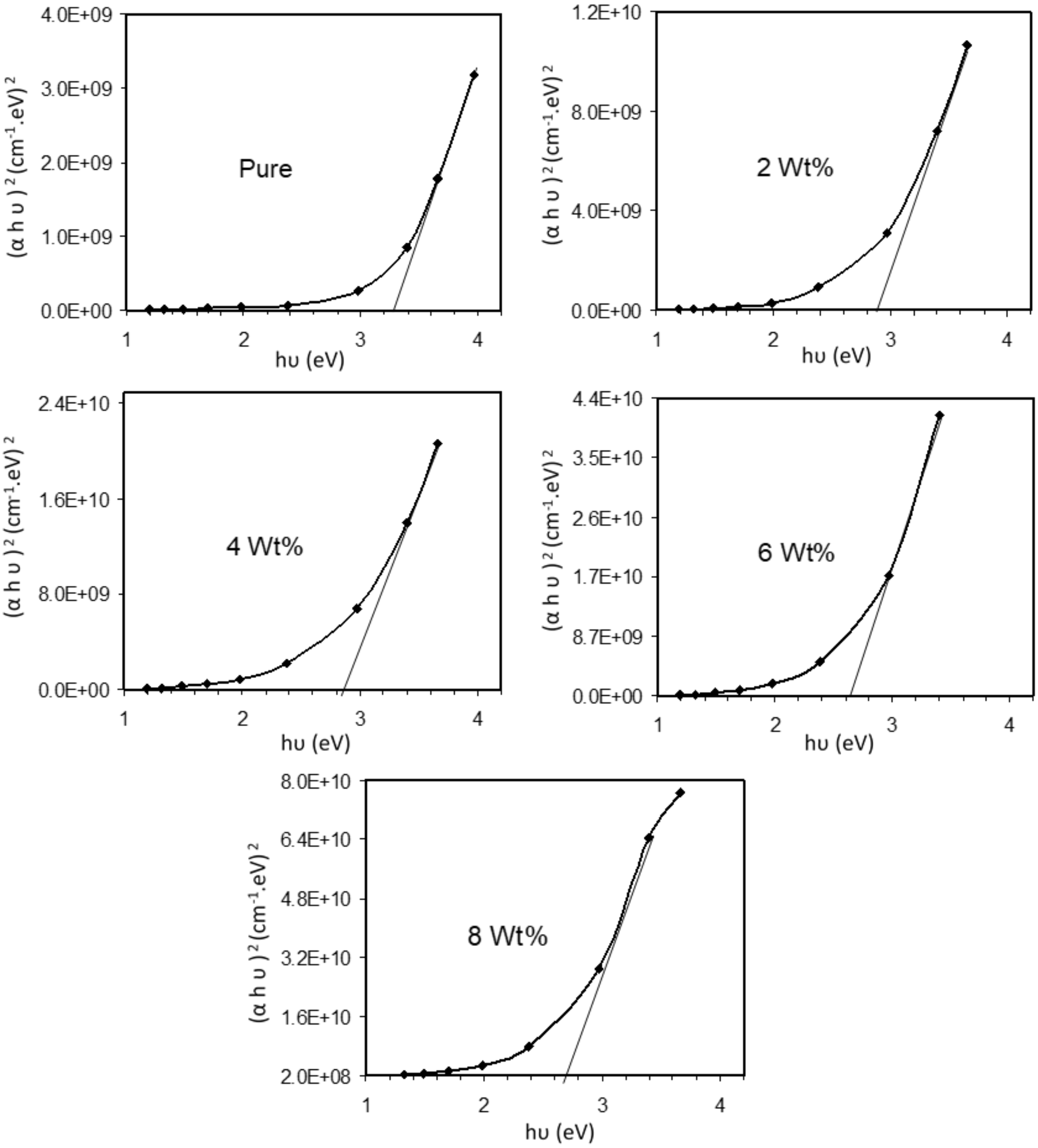

Figure (5). The relationship between $(\alpha h\upsilon)^2$ and the incident photon energy of pure and doped polyvinyl alcohol films.

It is shown in Figure 7., and noticed that when the wavelength changes, the refractive index also changes. But this change is irregular and depends on the doped percentages of potassium permanganate, where when the pure polyvinyl alcohol films, the refractive index increases with the wavelength with a regular increase, but when the films are doped with 8 wt% of potassium permanganate, it starts to increase at short wavelengths, then decreases and increases, once again. This behavior has been attributed to the formation of clusters and agglomerates of permanganate particles throughout the matrix [19].

Moreover, the refractive index is closely related to the reflectance and this is demonstrated by equation (4). Thus, the inversion effect is independent of the grafting effect within the polymer matrix [21]

The mechanism of absorbing energy the incident photon on samples causes the charges polarization, and the way in which interactions of light with the samples in most statuses is described through the complex dielectric constant ε *, which consists of two real and imaginary parts $\varepsilon^* = \varepsilon_r + \varepsilon_i$, Figure (8) shows the ε * of samples, the real value as a function of the wavelength of the pure and doped polyvinyl alcohol films, which was calculated from the equation [16]

$$\varepsilon_r = n^2 - k^2 \quad (5)$$

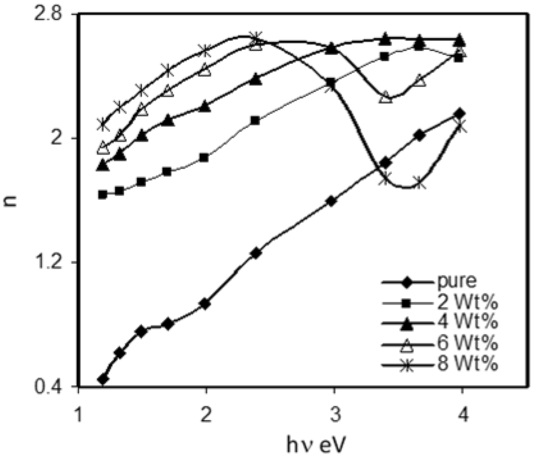

Figure (7). Refractive index as a function of incident photon energy for pure and doped polyvinyl alcohol films.

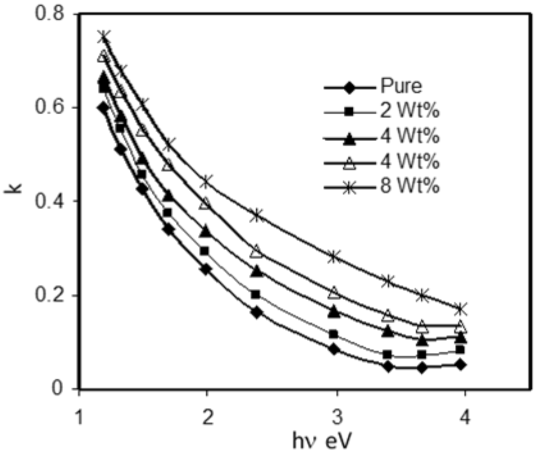

Figure (6). The extinction coefficient as a function of the incident photon for pure and doped polyvinyl alcohol films.

While Figure (9) shows the imaginary part of ε * as a function of wavelength for pure and doped polyvinyl alcohol films with different ratios of potassium permanganate, which was calculated from equation [16].

$$\varepsilon_i = 2nk \quad (6)$$

Noticed that the attitude of the real and imaginary ε * is similar to the behavior of the refractive index and the quenching coefficient, and this is evident through equations 5 and 6.

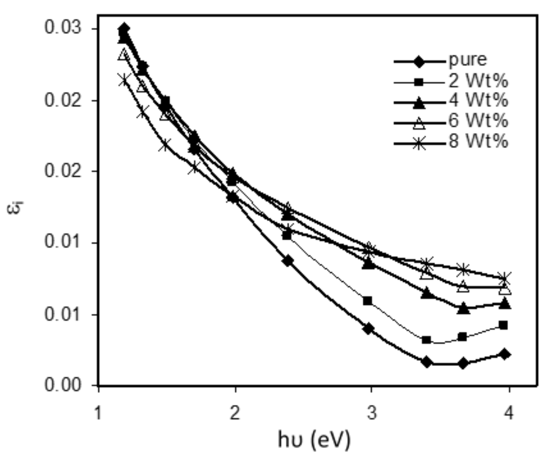

Figure (9). Imaginary dielectric constant as a function of incident photon energy for pure and doped polyvinyl alcohol films.

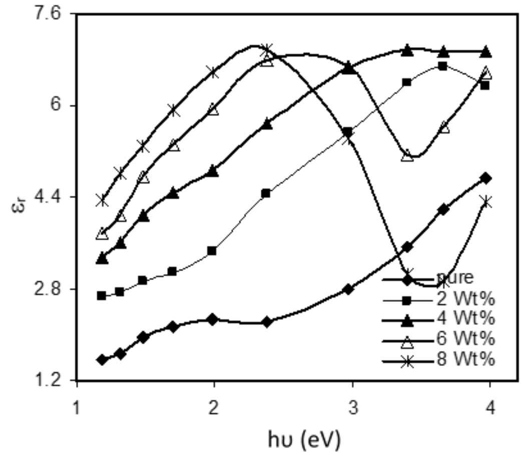

Figure (8). Real dielectric constant as a function of incident photon energy for pure and doped polyvinyl alcohol films.

The below equation was used to compute optical conductance [22]:

$$\sigma_o = \frac{\alpha n c}{4\pi} \qquad (7)$$

where σ_o is the optical conductivity and c is the speed of light.

Figure 10 shows the σ_o as a function of the hν for pure and doped polyvinyl alcohol films, and from it noted that the pure films have the highest values of optical conductivity at high energies, i.e. at ultraviolet wavelengths, unlike the doped films, which have higher optical conductivity at low energies, that is, at long wavelengths of visible light, and this is due to the high absorbance resulting from doping with potassium permanganate.

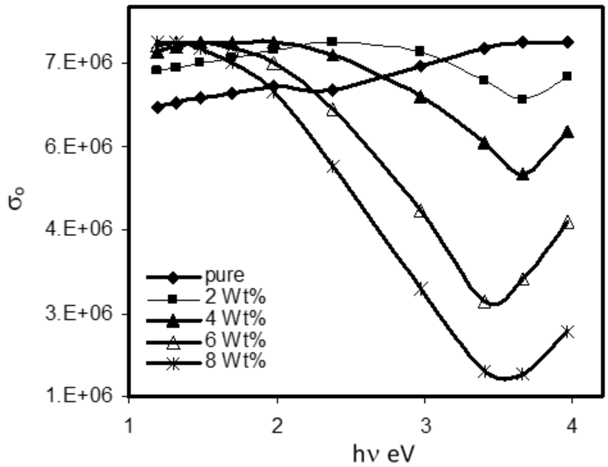

Figure (9). Optical conductivity as a function of incident photon energy for pure and doped polyvinyl alcohol films.

4. Conclusion

Concluded from the above that it is possible to successfully prepare films with good homogeneity from pure polyvinyl alcohol polymer and doped with different ratios of potassium permanganate by casting method. The inoculation process with different weight ratios of potassium permanganate had a clear effect on the functional groups of polyvinyl alcohol and also led to an improvement in the optical properties of the prepared films in terms of increasing the absorption coefficient and decreasing the optical energy gap of the prepared samples.

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