

**Study The Effect of Manganese Sulphate Monohydrate on Optical
Properties of Polyvinyl Alcohol (PVA)**

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Abstract

The present work is concerned to study the optical properties of polyvinyl alcohol (PVA) and Manganese sulphate monohydrate ($MnSO_4.H_2O$) films. Casting method used to prepare with different concentration of Manganese sulphate monohydrate. The absorption and transmission spectra have been recorded at the wavelength ranges (200-900) nm by using (UV-Visible) spectrophotometer. The results show that (The absorption coefficient, extinction coefficient and energy gap of the indirect allowed and forbidden transition) vary with the concentration of $MnSO_4.H_2O$ dopant.

الخلاصة

في العمل الحالي تم دراسة الخصائص البصرية لافلام بولي فينيل الكحول وكبريتات المنغنيز المائي وقد تم تحضير التراكيز المختلفه بطريقة الصب. وقد سجل طيف الامتصاصيه والنفاذيه للاطوال الموجيه التي تتراوح ما بين (٢٠٠-٩٠٠) نانومتر باستخدام مطياف (الاشعه فوق

البنفسجيه- المرئيه). وقد اظهرت النتائج ان معامل الامتصاص ومعامل الخمود وفجوة الطاقه للانتقال غير مباشر المسموح والممنوع تتغير بتغير تركيز الشائبه.

Key word: optical properties, polyvinyl alcohol, Manganese sulphate monohydrate effect of doping ratio, casting technique

1. Introduction

Optical properties of polymers constitute an important aspects in study of electronic transition and the possibility of their application as optical filters, a cover in solar collection, selection surfaces and green house [1]. Poly vinyl alcohol is a polymer with carbon chain back bone with hydroxyl groups attached to methane carbons, these OH-groups can be a source of hydrogen bonding and hence assist in the formation of polymer [2] that showed in figure (1) [3]. Poly vinyl alcohol(PVA) has several interesting physical properties, which are very useful in material science and technical applications. PVA, as semi crystalline water soluble material exhibits Certain physical properties resulting from crystal-amorphous interfacial effects [4].

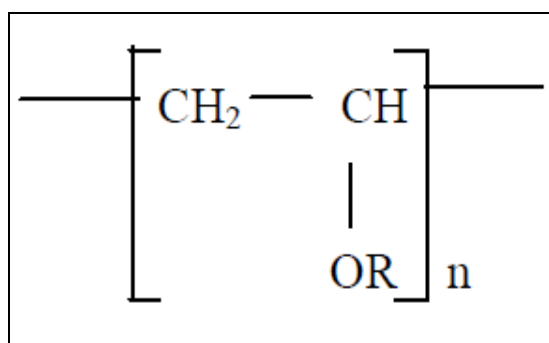


Fig.(1) The chemical structure of polyvinyl-alcohol [3]

Many studies have addressed PVA such as Omed and Dlear [5], studied optical absorption of PVA films doped with Nickel Chloride and they concluded that the optical energy gap is due to the direct and indirect allowed optical transitions and the energy gap decreases with increasing

NiCl₂ content. Mustafa *et al.*[6], studied the optical properties of (Polyvinyl alcohol) doped Cupper Chloride and showed that the energy gap is due to allowed direct transition and it decrease with increase the concentration of cupper chloride. the aim of this work is to study the optical properties of PVA films doped with different concentrations of Manganese sulphate monohydrate.

2. Experimental Part

PVA was obtained from Aldrich (90.98% degree of hydrolysis, $M_m=160000$).The (PVA) polymer was doped with MnSO₄.H₂O with 99% purity by mixing suitable volumes of (2, 5, 10, 15) Wt.% of MnSO₄.H₂O in PVA aqueous solution. Polymer films were obtained by casting, solutions on to glass plate. After solvent evaporation, the samples were dried in vacuum at room temperature. The films were ready which cut into pieces for characterization by measuring the absorption and transmission by using UV-Visible spectrophotometer type (T70/T80 Series UV/Vis Spectrometer).

3.Results and discussion:

Figure (1) shows the absorption spectrum of (PVA-MnSO₄.H₂O) films as a function of the wavelength of the incident light. The figure shown that no shift in the peak position while the intensity of these peaks increased as an increase the concentration of Manganese sulphate monohydrate. Which means the addition to pure polymer does not change the chemical structure of the material but new physical mixture is formed. These results are results reached by the researcher [7]. similar to the

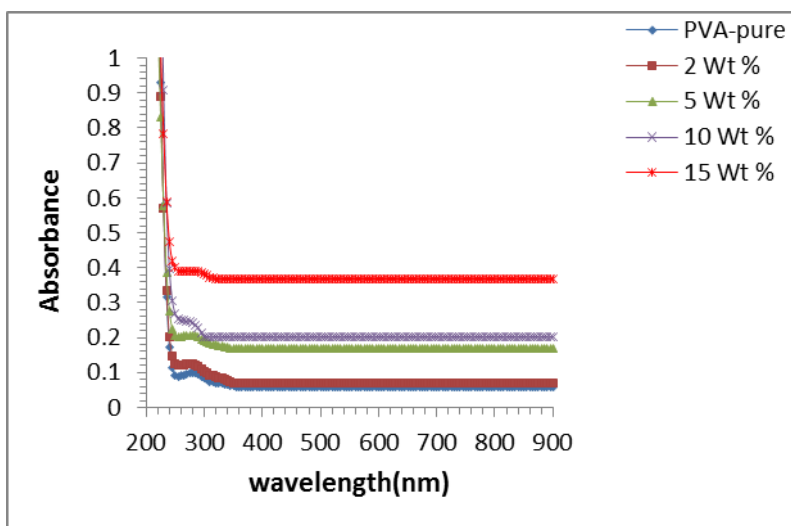


Figure (1): The absorbance as function of wavelength for (PVA- MnSO₄. H₂O) films

Figure (2) shows the optical transmittance spectrum as a function of wavelength by adding different rate of MnSO₄.H₂O .The transmittance percent decreases with increasing doping ratio of MnSO₄.H₂O.

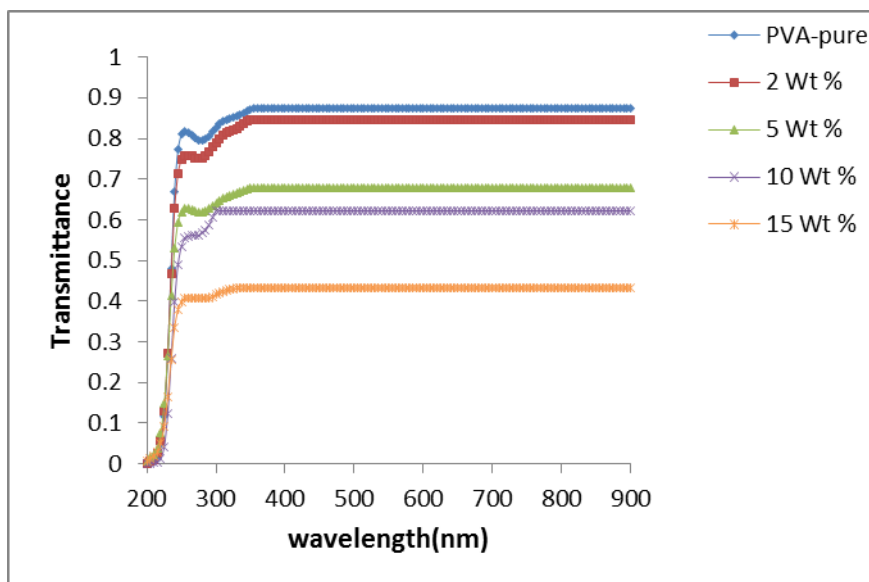


Figure (2): The transmittance as function of wavelength for (PVA- MnSO₄. H₂O) films

Figure (3) shows the reflectance spectrum as a function of wavelength for (PVA-MnSO₄.H₂O) films, reflection spectrum is calculated from absorption and transmission spectrum according to eq.

$$R+A+T=1$$

The reflectance as shown in figure (3) increases with increasing the additives of MnSO₄.H₂O in the film.

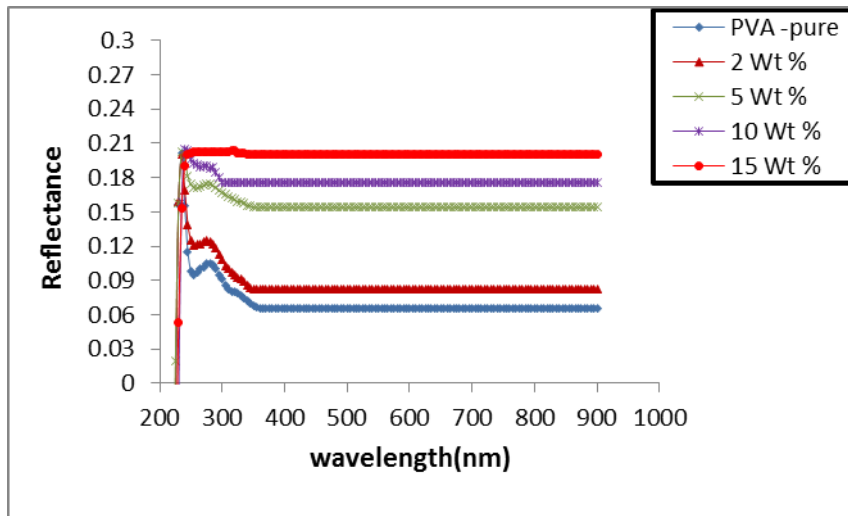


Figure (3): the reflectance spectrum as a function of wavelength for (PVA-MnSO₄.H₂O) films

The absorption coefficient (α) was calculated in the fundamental absorption region from the following equation [8]:

$$\alpha = 2.303 \frac{A}{d}$$

Where: (A) absorbance ; (d) the thickness of sample.

Figure (4) shows the absorption coefficient α (cm)⁻¹ as a function of photon energy for (PVA-MnSO₄.H₂O) films. we note the change in the

absorption coefficient is small at low energies this is indicates the possibility of electronic transitions is a few. At high energy, the change of absorption coefficient is large this is indicates the large probability of electronic transitions are the absorption edge of the region [8]. The absorption coefficient helps to conclude the nature of electronic transitions, when the high absorption coefficient values ($\alpha > 10^4 \text{ cm}^{-1}$) at high energies we expected direct electronic transitions, and the energy and the momentum preserve of the electron and photon, when the values of absorption coefficient is low ($\alpha < 10^4 \text{ cm}^{-1}$) at low energies we expected in this case indirect electronic transitions, the momentum of the electron and photon preserves by phonon helps. The results showed that the values of absorption coefficient of the (PVA-MnSO₄.H₂O) films less than 10^4 cm^{-1} which indicates to the indirect electronic transition.

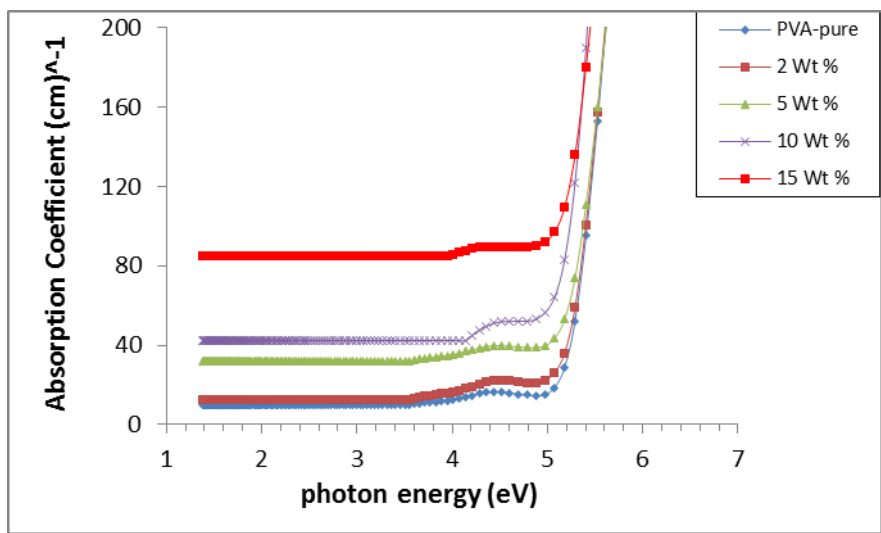


Figure (4): the absorption coefficient $\alpha \text{ (cm)}^{-1}$ as a function of photon energy (eV) for (PVA-MnSO₄.H₂O)films

Both the allowed and forbidden indirect transition band energy gap have been calculated by using equation.

$$\alpha h\nu = B(h\nu - E_g^{opt.} \pm E_{ph.})^r$$

Where: $E_{ph.}$: energy of phonon, is (-) when phonon absorption, and (+) when phonon emission.

($r = 2$) for the allowed indirect transition.

($r = 3$) for the forbidden indirect transition.

When the value of $r = 2$, the allowed indirect transition band energy gap is calculated, but when the value of $r = 3$, the forbidden indirect transition band energy gap is calculated.

Figure (5) shows the relation between absorption edge $(\alpha h\nu)^{1/2}$ for (PVA-MnSO₄.H₂O) as a function of photon energy, on drawing straight line from the upper part of the curve toward the (x) axis at the value $(\alpha h\nu)^{1/2} = 0$ we get the energy gap for the allowed indirect transition. The obtained values are shown in table (1). We can see that the values of energy gap decrease with the increasing of the weight percentages of Manganese sulphate monohydrate. This attributed to the creation of site levels in the forbidden energy gap, the transition in this case is conducted in two stages that involve the transition of electron from the valence band to the local levels to the conduction band as a result of increasing the manganese sulphate monohydrate weight percentage. These results are similar to

the results reached by the researchers [9]. The forbidden transition of the indirect energy gap is calculated in the same way, and the values of the indirect energy gap for the (PVA-MnSO₄.H₂O) films are shown in table (1). Figure (6) shows the forbidden transition of the indirect energy gap for the (PVA- MnSO₄.H₂O) films.

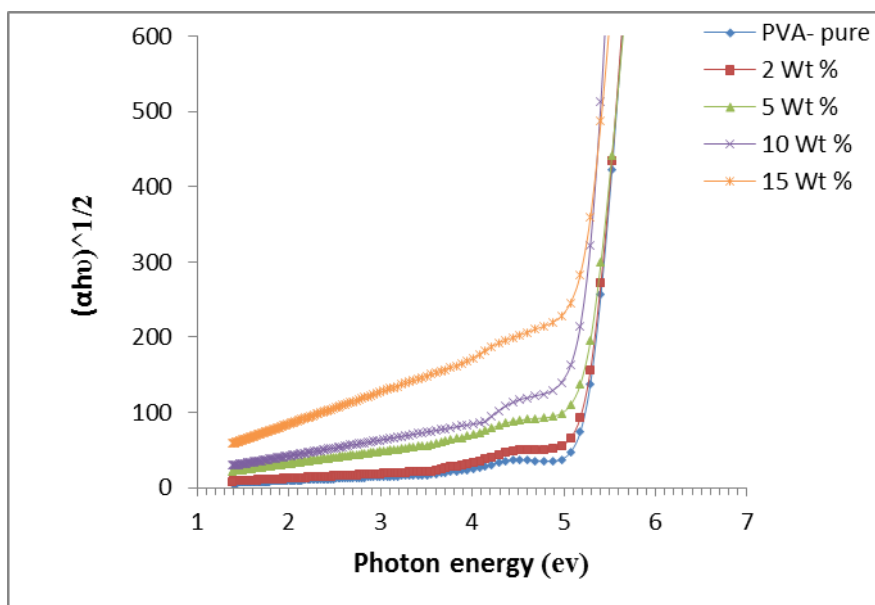


Figure (5) : The energy gap for the allowed indirect transition as a function of photon energy of (PVA-MnSo₄.H₂o) films.

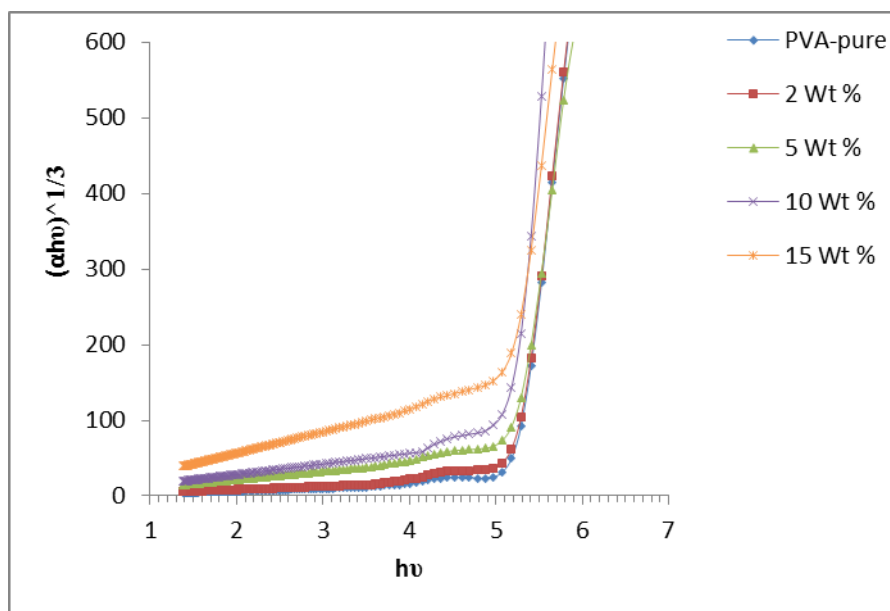


Figure (6) : The energy gap for the forbidden indirect transition as a function of photon energy of (PVA-MnSo₄.H₂o) film

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Table (1) The values of energy gap for the allowed and forbidden indirect transition

(MnSO₄.H₂O) Wt. %	The values of optical energy gap for the indirect transition (ev)	
	allowed	forbidden
0	5.1	5.05
2	5.08	5
5	5.03	4.95
10	5	4.9
15	4.9	4.85

The attenuation coefficient (k) is directly proportional to the absorption coefficient (α):

$$k = \alpha \lambda / 4\pi$$

that means the extinction coefficient increase with increasing doping ratio of MnSO₄. H₂O, as shown in figure (8).

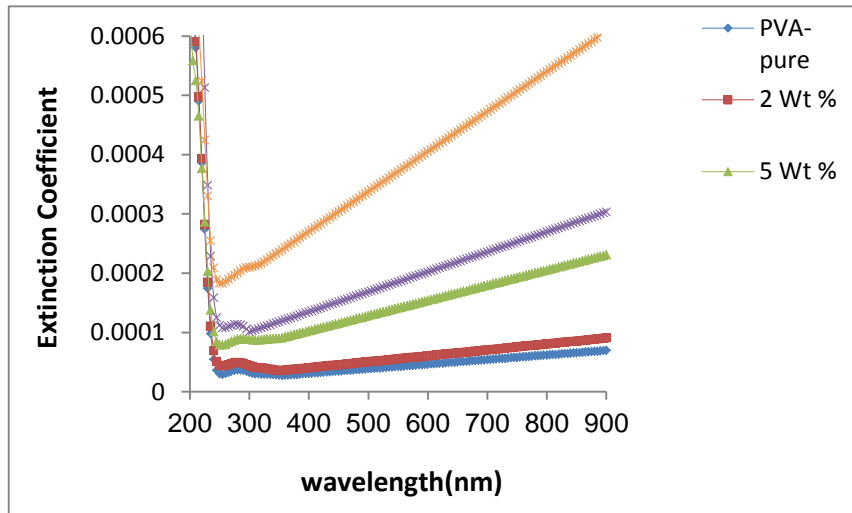


Figure (8): Extinction coefficient as a function of wavelength of (PVA-MnSO₄.H₂O) films

The real (ϵ_r) and imaginary (ϵ_i) parts of dielectric constants were calculated from the following equations:

$$\epsilon_r = n^2 - k^2$$

$$\epsilon_i = 2nk$$

Figures (9) and (10) shows the variation of real (ϵ_r) and imaginary (ϵ_i) parts of dielectric constants of (PVA-MnSO₄. H₂O) films .It is concluded that the variation of ϵ_r mainly depends on n^2 because of small values of k^2 , while ϵ_i mainly depends on the k values which are related to the variation of absorption coefficients [10].

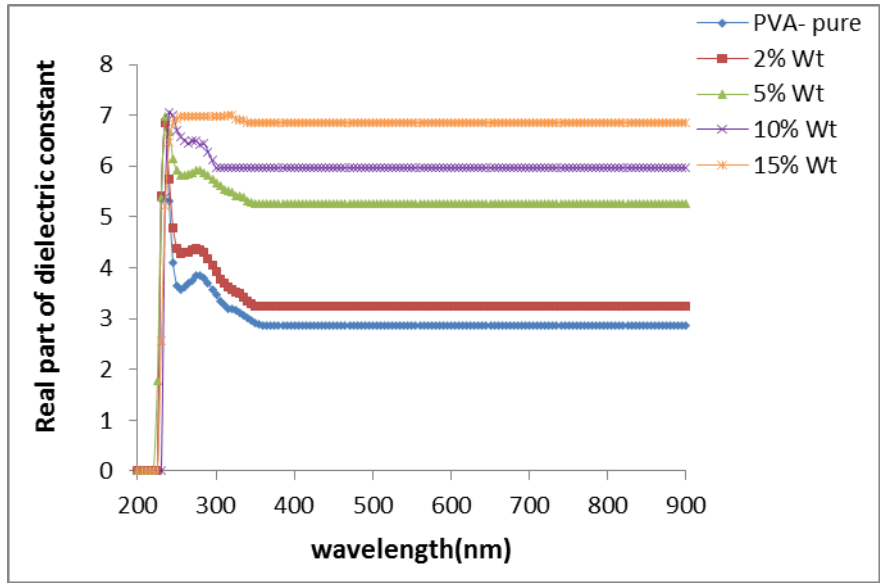


Figure (8): The real dielectric constant (ϵ_r) as a function of incident wavelength (PVA-MnSO₄.H₂O) films.

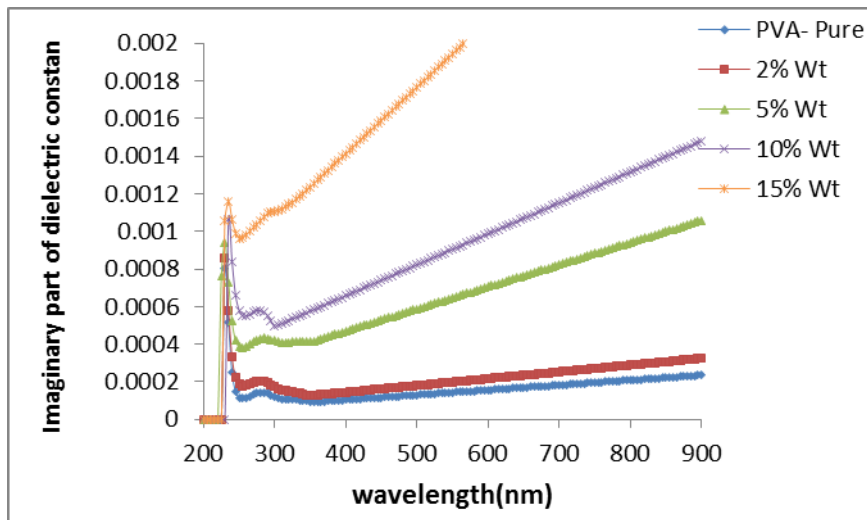


Figure (9): The imaginary dielectric constant (ϵ_i) as a function of incident wavelength (PVA-MnSO₄.H₂O) films.

Conclusion:

From this study, we can concluded that the addition of Manganese sulphate monohydrate effect on optical properties of PVA films. The energy gap for PVA polymer decreased with increasing doping ratio of MnSO₄.H₂O for allowed and forbidden indirect transition.

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