

**Optical Properties Of poly vinyl alcohol (PVA) doped with Ali
Zarin Orange Azo Dye thin films prepared by cast method**

Hassan. K. Ibrahim and Rusel D . Salem

physics Department , College of Education , University of Basrah .

Email: rosal404@Yahoo.com

Abstract:

In this study the optical properties of poly vinyl Alcohol (PVA) doped with AliZarin orange Azo dye thin films of different thickness were deposited on glass substrate at room temperature by using cast method technique . The optical properties investigated include their absorbance spectra , transmittance ,absorption coefficient , reflectance spectra ,band gap, extinction coefficient , optical conductivity , refractive index, and complex dielectric constant . the absorbance of the films were found to be high in the visible region for all the thicknesses with peaks around 400nm , However the absorbance of the films were found to exhibit low values near infrared region . The thickness of the films causes important changes in the optical properties of all parameters were investigated under this study .

Key word: (PVA) polymer, alizarin orange Azo dye, absorption coefficient, transmittance, complex dielectric constant , optical conductivity .

الخلاصة:

تم في هذا البحث دراسة الخواص الضوئية للبوليمر بولي فنيل الكحول المشوب بصبغة البزارين البرتقالية اللون بواسطة أفلام محضره بطريقة الصب على شرائح من الزجاج تم الاعتماد على طيف النفاذية لحساب الخواص الضوئية مثل معامل الامتصاص , معامل الانكسار , معامل الخمود , التوصيلية الضوئية , الأجزاء الحقيقية والخيالية لثابت العزل , فجوة الطاقة . أظهرت الأفلام المحضرة قيم عالية للنفاذية والانعكاسية عند الأطوال الموجية (550-1300) نانو متر . لقد لوحظ انخفاض كل من الامتصاصية , معامل الامتصاص , معامل الخمود , معامل الانكسار مع الطول الموجي وخاصة عند المنطقة القريبة من طيف الأشعة تحت الحمراء . لقد أظهرت الدراسة زيادة كل من معامل الامتصاص , معامل الخمود , التوصيلية الضوئية , الأجزاء الحقيقية والخيالية لثابت العزل لطاقة الفوتون ولكن كل من معامل الانكسار ومعامل الخمود , الانعكاسية تقل مع زيادة طاقة الفوتون . أوضحت الدراسة بان زيادة السمك يعمل على زيادة الامتصاصية والانعكاسية ولكنه يقلل النفاذية وذلك كلما زاد الطول الموجي . تم حساب فجوة الطاقة الغير مباشرة للأفلام المحضرة .

Introduction:

A great interest have been explored in the field of conductive and Semiconductive polymeric materials due to the fast progress in the molecular applications ,these researches have been made to obtain a new polymeric materials with enhanced specific properties for specific application or better combination of different properties [1,2] . Amongst the new classes of materials , polymers are especially interesting because they combine the optical and electronic properties of semiconductors with the processing advantages and mechanical properties of polymers [3] . The study of the optical absorption Spectra in solids provides essential information about the band structure and the energy gap in the crystalline And non – crystalline materials [4]. The analysis of the absorption spectra in the lower energy part gives information about atomic vibration while the higher energy part of the spectrum gives knowledge about the electronic states in atom [5]. Optical properties such as refractive indices for certain range of wavelength between ultraviolet and near infrared , and optical band gap values becoming quite important criteria for selection of application of the fabricated films , the refractive indices of optical materials are considerable importance for applications in integrated optic devices such as switches [6] . In recent years , ,there has been considerable interest in use of thin films in solar cell devices such as zinc sulphide (Z_nS) when

doped with copper or other ions[7] . In the Present the optical properties of Poly Vinyle Alcohol (PVA) doped with Alizarin orange Azo dye thin films were studied in different thicknesses in the wavelength (300-1300) nm have been investigated. The study include measurement of optical spectra , absorption spectra , transmission spectra , absorption coefficient , refractive index , reflectance, extinction coefficient , optical band gap , optical conductivity , and complex dielectric constant for different film thickness. The absorption coefficient near fundamental absorption edge in both of crystalline and amorphous semiconductors is dependent on the photon energy . For direct transitions the absorption coefficient was taken on the following more general form as a function of photon energy [9]

$$\alpha h \nu = A (\alpha h \nu - E_g)^n \dots\dots 1$$

and for indirect transition

$$\alpha h \nu = B (\alpha h \nu - E_g)^n \dots\dots 2$$

where ν is the frequency of the incident photon , n is the number which characterizes the optical processes .n has the value 1/2 for the direct allowed transition , 3/2 for a forbidden direct allowed transition and 2 for the indirect allowed transition , A and B are constants , and E_g is the optical energy gap. when the straight portion of the graph of $(\alpha h\nu)^n$ against $h\nu$ is extrapolated to $\alpha = 0$ the intercept gives the transition band gap [10] . From transmission (T) and the

thickness of polymer (d) the absorption coefficient (α) is calculated according to equation (3) given in reference [11,12]

$$\alpha = (2.303/d) \log(1/T) \longrightarrow 3$$

where d is the thickness of polymer .

The optical constant for semiconductors and insulators are obtainable from the following relationship [13] if the absorption coefficient α and the bulk reflectance R are known .

$$R + T + A = 1 \dots\dots\dots 4$$

$$R = (n-1)^2 / (n+1)^2 \longrightarrow 5$$

Where n is refractive index of the polymer .The extinction coefficient K could be found using the following relation [14] .

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

Where λ is the wavelength of electromagnetic wave and α is the absorption coefficient of the films .The relationship between complex dielectric constant (ϵ) and extinction coefficient (K) is given by [15]

$$\epsilon = \epsilon_r + \epsilon_i = (n + iK)^2 \longrightarrow 6$$

Where

$$\epsilon_r = n^2 - k^2 \text{ and } \epsilon_i = 2nk \longrightarrow 7$$

Where ϵ_r and ϵ_i are the real and imaginary part of the dielectric constant respectively .

The optical conductivity σ_0 is given by [16]

$$\sigma_0 = \alpha n c / 4 \pi \longrightarrow 8$$

Where c is the velocity of light .

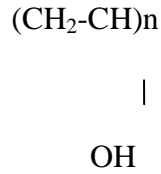
The experimental part :

Poly Vinyl Alcohol (PVA) was prepared and condensation polymerization adopting to method previously reported [8] .

0.01 Mole of polymer (1.5 gm)is first dissolved in 10 mil of Methanol solvent with stirred at room temperature for 5-7h 0.1 Mole of AliZarin Orange Azo dye (0.266)gm was dissolved in 5 mil of dimethyle formamid (DMF) with stirred at room temperature for (4-5)h . Then the dopant was added to the polymer with ratio 30% percentage. The stirred solution was casted on the glass substrate cited horizontally to get homogeneous thickness . The important thing before the deposition of films is the careful cleaning Of the glass substrate which is cleaned by using organic solvent such as- ethanol , methanol , Acetone ect . Finally the glass substrate were dried before use . The solvent is allowed to evaporate slowly at room temperature . Current process was applied to the samples as a final process Via increasing the temperature in the rate 10 c° /hr up to 70 c° , then cooled gradually up to the room temperature.

Results and discussion :

Fig (1) shows the expected structure of polymer under the present study .



Fig(1) : The expected chemical structure of polymer .

The optical properties of poly vinyl Alcohol (PVA) doped with Alizarin orange Azo dye thin films were determined from absorbance and transmission measurements in the range of (300 – 1300) nm . Fig (2) : shows the absorbance spectra of the thin films of (PVA) doped With Alizarin orange Azo dye in different thicknesses . These spectra reveal that the films have peak absorbance recognized around ($\lambda = 400$ nm) , However the absorbance were increased with increasing of wavelength From (300 - 400) nm and then decreased rapidly in the range of (400 – 520)nm after that the absorbance remain constant until 1300 nm . One can be concluded that the effect of thickness were increased the absorbance from (1.4 - 2.3) when the thickness increased from (6-8) μm . this is because of the reason that in case of thicker films more atoms are present in the film so more states will be available for the photons to be absorbed .

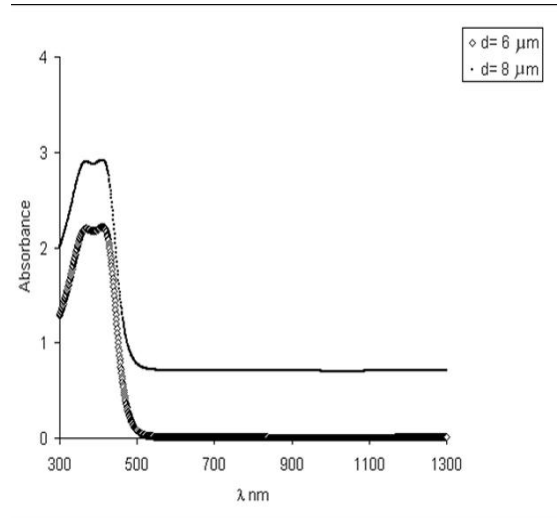


Fig (2) Absorbance versus wavelength of incident radiation obtained at room temperature

Fig(3):shows the transmission spectra of the films prepared by cast method for thicknesses varying from (6-8) μm . The films showed optical transmission (78- 96)% in the range(520-1300)nm, But the optical transmission were decreased rapidly in the wavelength less than 520nm until the wavelength 300nm for all the films thicknesses. It has been observed that all T% increase with decrease in the films thicknesses because of the increase of thicknesses causes decrease in the transmittance.

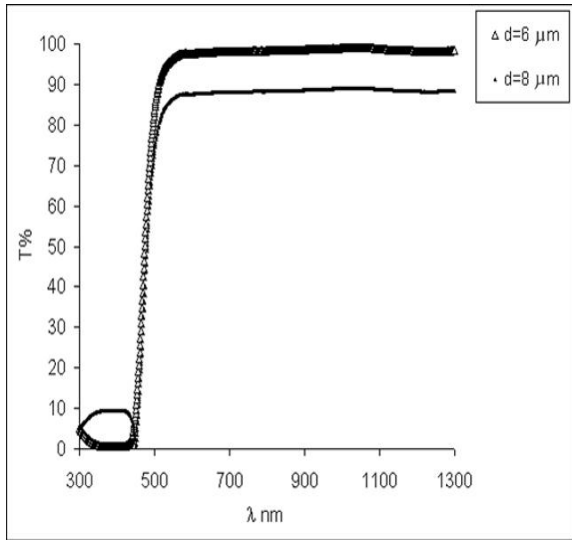


Fig (3) The transmission spectra for (PVA) doped with alizarin orange films with different thicknesses

because of the increase of thicknesses causes decrease in the transmittance .

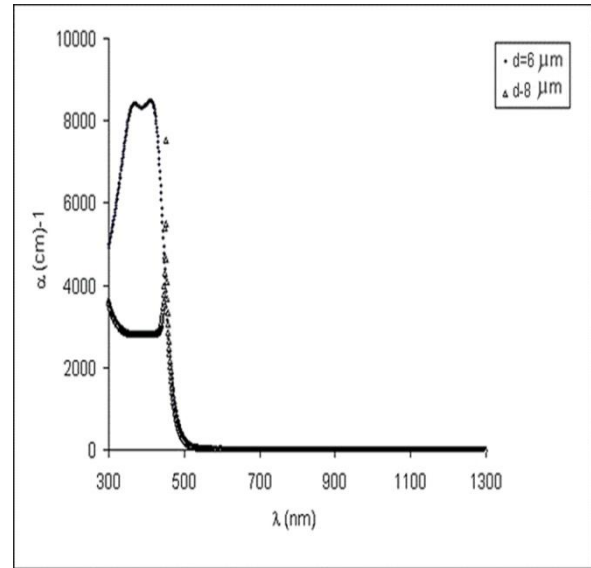


Fig (4) The relationship between absorption coefficient and wavelength

Fig(4) : shows the relation between absorption coefficient and wavelength , from this figure it can be shown that the absorption coefficient (α) was decreased with increasing of wavelength However the high value of absorption coefficient (\square) corresponding to the lower value of the thicknesses and this fact agree with the equ.3. . The dependence of absorption coefficient (α) on the photon energy is important in studying energy band structure and the type of transition of the electron . The absorption coefficient (α) was estimated by the transmittance data as shown in figure (5) when $d = 6 \mu\text{m}$. The absorption coefficient (α) remain constant in the range (1.1 – 2.25) ev and then rise sharply with maximum peak around ($h\nu = 2.5 \text{ ev}$) , above 2.5 ev there is a sharp fall in the absorption coefficient , a similar behavior observed when $d= 8 \mu\text{m}$ But the maximum peak recorded around ($h\nu = 3 \text{ ev}$), that is

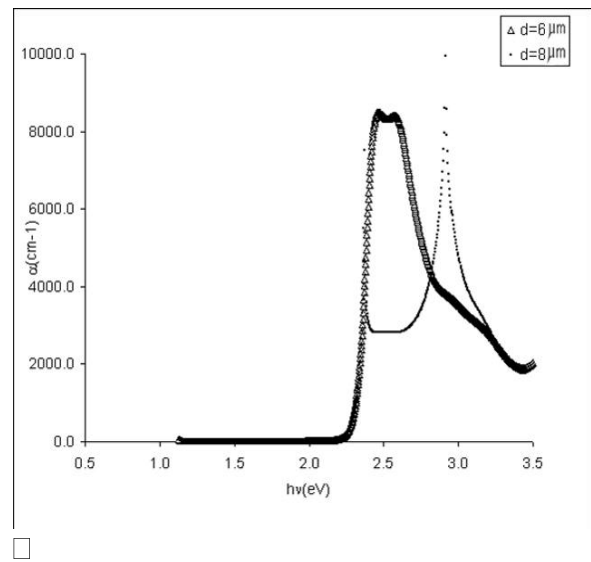


Fig (5) The relationship between absorption coefficient and photon energy

Fig (6) : shows the plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ (ev) for indirect transition. The indirect energy gaps E_g were determined from these curves and

given with value of $E_g = 2.3$ eV with phonon energy $E_p = 2.1$ eV for ($d = 6 \mu\text{m}$) and value of $E_g = 2.25$ eV for $d = 8 \mu\text{m}$ with phonon energy $E_p = 1.75$ eV . It is evident that the increase in thickness lead to decrease in optical band gap and phonon energy . Similar behavior observed by others [17]

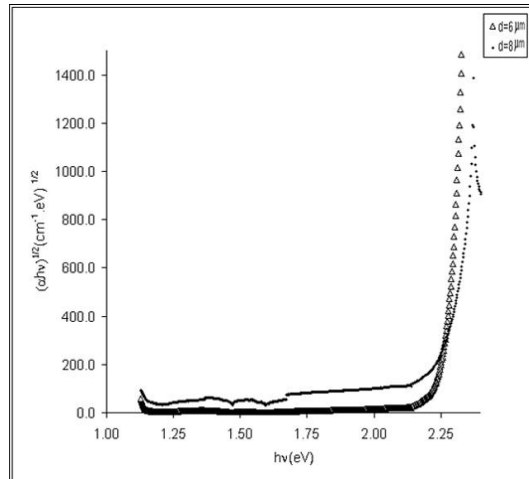


Fig (6) $(\alpha h\nu)^{1/2}$ Versus $h\nu$

Fig (7) : shows the relation between reflectance (R) and wavelength of incident radiation , it is clear from the figure that the reflectance was increased widely in the wave length between (350-500) nm to reach 85% when $d = 8 \mu\text{m}$ and 95% when $d = 6 \mu\text{m}$.The reflectance remain constant at wave length Longer than 550 nm for all thicknesses . The dependence of reflectance (R) on the photon energy ($h\nu$) as shown in Fig (8) . It is clear form the figure that the reflectance was independent on photon energy below 2 eV . But the reflectance decreased rapidly when ($h\nu$) longer than 2 eV . One can be conclude that the reflectance was increased with decreasing of thicknesses. This effect

was agreement with the theoretical equ.4 .

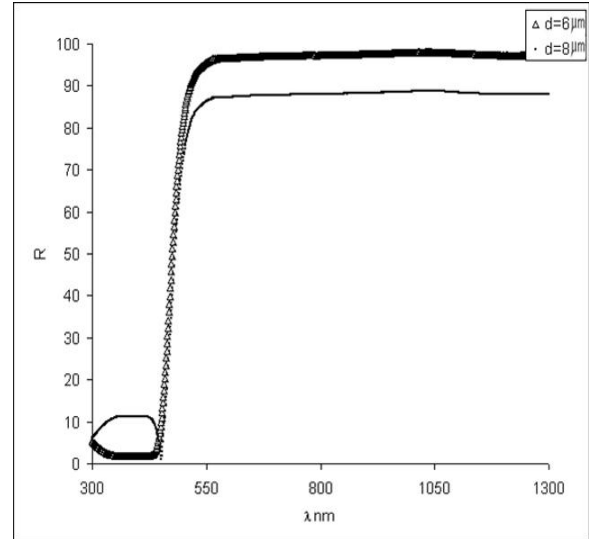


Fig (7) Reflectance versus wavelength of incident radiation

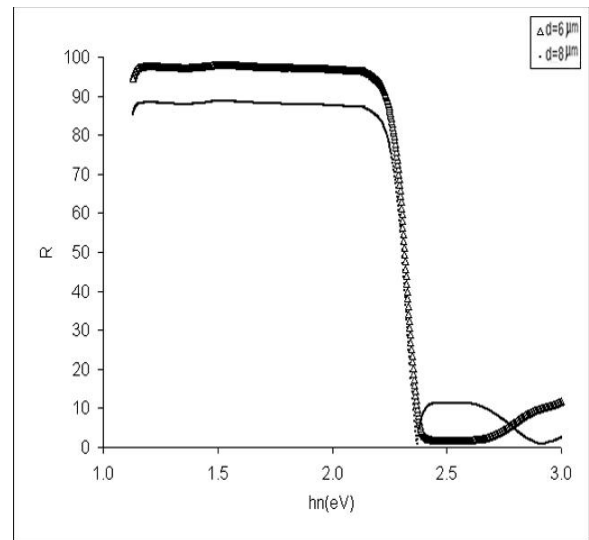


Fig (8) Reflectance versus photon energy ($h\nu$)

Fig (9) : shows the relation between extinction coefficient (k) and wave length , the extinction coefficient was decreased rapidly in the wavelength between (300 – 500) nm, but above ($\lambda=500$) nm the extinction coefficient remain constant . The extinction coefficient has been measured as a function of photon energy .The variation of extinction coefficient with photon energy is shown in Fig (10) .

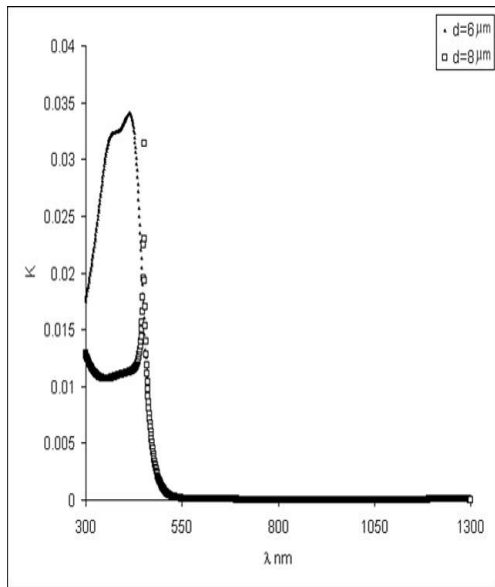


Fig (9) The relationship between extinction coefficient and wavelength

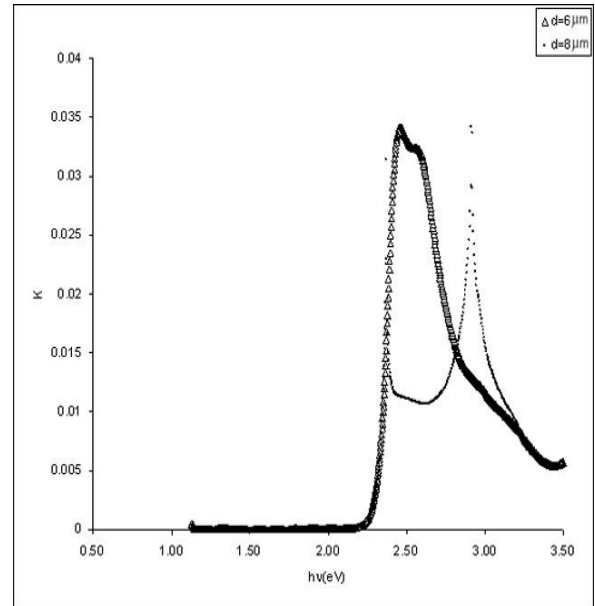


Fig (10) The relationship between extinction coefficient and photon energy

the rise and fall in the extinction coefficient is due to the variation in the absorbance. The refractive index dependence of the wave length has been calculated in the range between (300 -1300) nm as shown in fig (11) , the refractive index become constant in the wavelength greater than 550nm , but it was increased sharply in the short wave length below 550 nm.

Different curves were obtained because of variation of the film thicknesses .

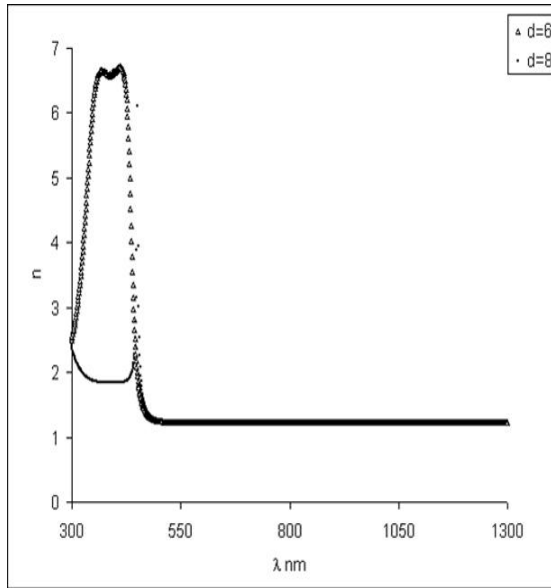


Fig (11) The refractive index versus wavelength

.Fig (12) : shows the relation between refractive index and photon energy, The refractive index become nearly constant in the photon energy larger than 1ev but it was increased rapidly when photon energy less than 1 ev . Different curves were obtained because of variation of the film thicknesses.

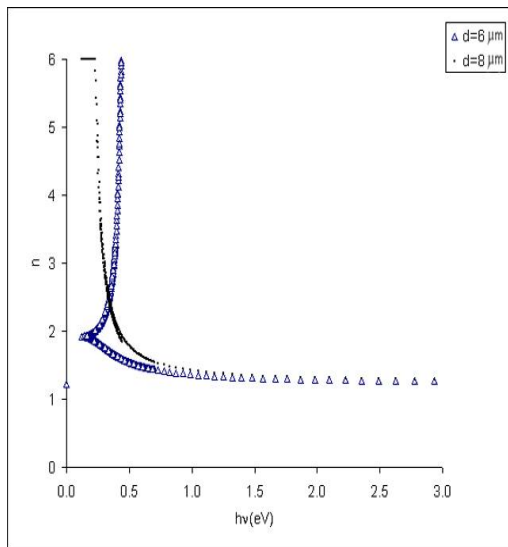


Fig (12) The refractive index versus photon energy

Fig (13) : shows the relation between optical conductivity and photon energy . The optical conductivity was determined using equation (8) . The high magnitude of optical conductivity ($1.5 \times 10^{12} \text{ sec}^{-1}$) confirms the presence of very high photo response of the film . The increased of optical conductivity at high photon energies is due to the high absorbance of (PVA) doped with Alizarin orange Azo dye thin film and may be due to electron excited by photon energy which also caused by the hopping of the charge carriers between the localized states and also due to the excitation of the charge carriers to the states in the conduction band . Similar behavior was observed with many polymers such as poly (p-Amino benzaldehyde) terminated by phenylene diamine thin film [18].

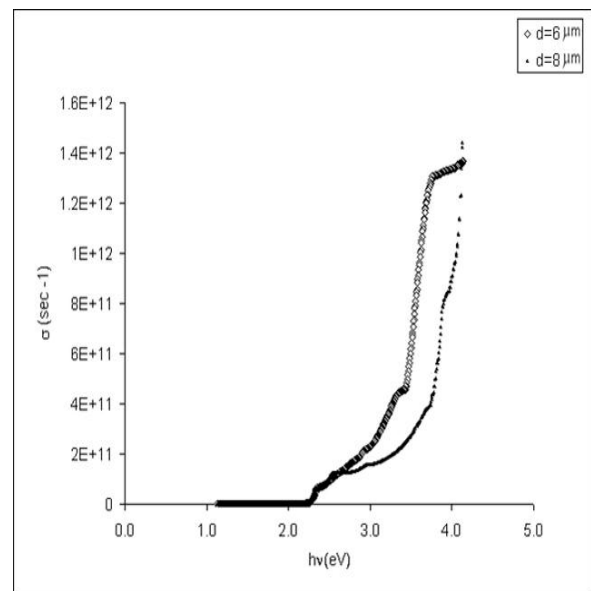


Fig (13) The relationship between optical conductivity and photon energy

Fig (14) : shows the relation between real part of dielectric constant (ϵ_r) And photon energy $h\nu$ (ev). In the range of (1-2) ev the real part of dielectric constant was independent on photon energy in this region which corresponding to the high wavelength . The real part of dielectric constant was increased sharply in the high photon energy greater than 2ev , similar behavior was observed by others [19].

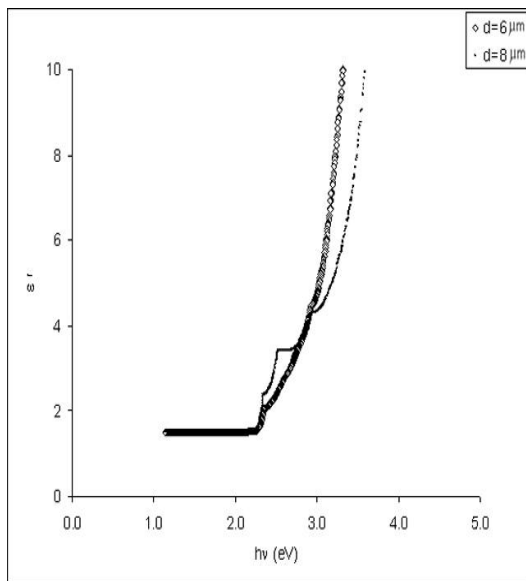


Fig (14) The relationship between real part of dielectric constant and photon energy

Fig (15) : shows the relation between imaginary part of dielectric constant (ϵ_i) and photon energy $h\nu$ (ev) it is clear from the figure that (ϵ_i) is independent on photon energy in the range (1-2.25) ev which corresponding the region in the high wavelength near infrared region , and then (ϵ_i) Was increased slowly in the rang (2.25 – 3.5)ev but (ϵ_i) was increased sharply when photon energy greater than 3.5 ev .The thicknesses of the films causes important changes in

real part and imaginary part of dielectric constant.

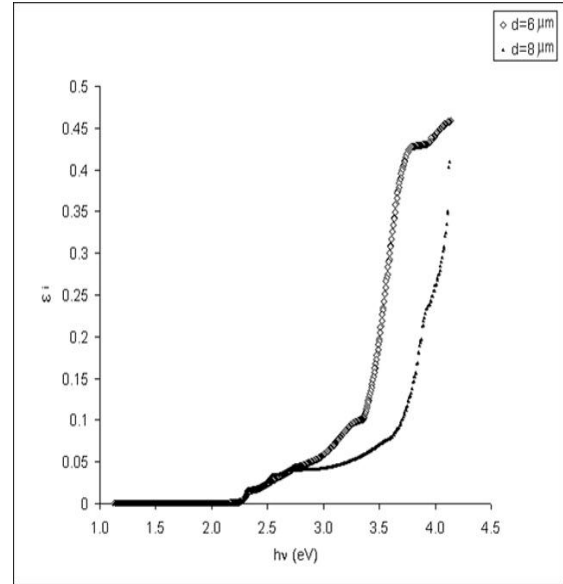


Fig (15) The relationship between imaginary part of dielectric constant and photon energy

Conclusion :

Poly Vinyle Alcohol (PVA) doped with alizarin orange thin films have been prepared by cast method technique .The optical transmission spectrum is used to calculate the optical properties i.e. absorption coefficient , refractive index , extinction on coefficient , optical conductivity , real and imaginary pants of dielectric constant and optical band gap . The films exhibited more transmission and reflectance at high wavelength (550 – 1300) nm . The absorbance , absorption coefficient , extinction coefficient , and refractive index were decreased with increasing

of wavelength especially near in the infrared region .The absorption coefficient , the extinction coefficient , optical conductivity , real and imaginary parts of dielectric constant were increased with increasing of photon energy .The refractive index the extinction coefficient and reflectance were decreased with increasing of photon energy . The effect of film thickness was increased the reflectance and absorbance but decreased the transmittance with increasing of wavelength indirect energy gap was calculated for the films.

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