Dispersion Parameters, Optical Constant and Photoluminescence of Poly Vinyl Alcohol Grafted Eosin –Y Dye (PVA-g-Ei)

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Abstract

Optical properties of PVA-g-Ei thin film prepared by cast method have been studied in spectral range of (200-900 nm) .The dispersion of the refractive index is discussed in term of Wlemple - DiDomenico single oscillator model , many dispersion parameters such as single oscillator energy (E_o), dispersion energy (E_d), refractive index ($n_{(0)}$), discussed using Miller's rule ,the optical absorption at the fundamental absorption edge dielectric constant (ε_∞) ,moment of the dielectric constant optical spectrum(M_{-1} ,M_{-3})and energy gap by Wimple-DiDomenico approximation (E_g^{WDD})have been calculated,non linear optical susceptibility ($\chi^{(3)}$) has been discussed , direct energy gap by Tauc relation (E_g^T), energy gap by absorption spectrum (E_g^A) and Urbach energy of the localized states (E_u) were also calculated . Photoluminescence spectrum of investigated PVA-g-Ei thin film has been recorded in spectral range of (500-700 nm) , photoluminescence quantum yield(Φ_{PL}) and the energy gap at the absorption peak (E_g^{PL}) have been also determined .

Keywords: Organic Eosin-Y dye, polyvinyl alcohol, optical parameters, Photoluminescence.

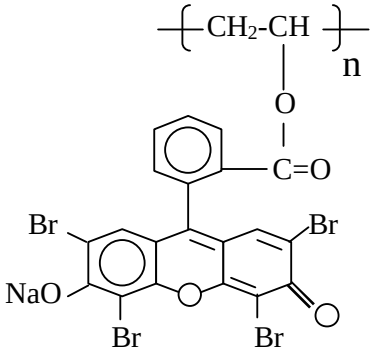
Introduction:

Amongst the new classes of materials, polymers are specially interesting because they combine the optical and electronic properties of semiconductors with the processing advantages and mechanical properties of polymers [1] . The selection of the appropriate optical or optoelectronic material for a particular application requires a firm understanding of its optical properties . Many applications require the material in thin form . Microscopic defect , which control surface smoothens and coating homogeneity, contribute to the scattering of light and associated degradation of the optical response .Similarly, structural disturbances at the atomic level can alter the optical properties through modifications to the complex refractive index of the material[2,3]. In the present work optical properties of new ester copolymer polyvinyl alcohol grafted Eosin-Y dye have been investigated to calculate many dispersion parameters such as E_o , E_d , $n(0)$, ε_∞ , M_{-1} ,M_{-3} , E_g^{WDD} also Photoluminescence spectrum measurement used to calculate quantum yield(Φ_{PL}) and the energy gap at the absorption peak E_g^{PL} .

Experimental:

Polyvinyl alcohol grafted Eosin-Y dye (PVA-g-Ei) has been synthesised and characterized according to the literature [4] .The structural diagram of copolymer is shown in Figure (1). To determine the optical properties of the copolymer,the (PVA-g-Ei) samples were prepared dissolving 0.5 g of copolymer in 5 ml of dimethylsulfoxide(DMSO) provided by Aldrich . All specimens are prepared by using cast method on corning 7059 glass substrates .

cleaned by immersing them in cleaning solution [10% $K_2Cr_2O_7$ + H_2SO_4] [5]for 1hr in ultrasonic bath then washed with distilled water and organic solvent such as ethanol ,acetone …etc. , followed by nitrogen gas in a glove box . Glass substrates dimensions were about (25x10)mm. Thermospectronic model HEλIOSα v 4.60 serial No. 102024 was used to measure the optical parameters .Photoluminescence spectrum was recorded by using Spectrofluorometer model (RF-540)by SHIMADZU Co.



Figure(1): The polymer structure diagram

Results and discussion:

The absorption and the transmittance(T) spectra for PVA-g-Ei thin film were recorded in the wavelength range of (200-900nm) .The reflection (R) can be determined using the following relation[6] :

$$T = \frac{(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}} \quad \text{……..(1)}$$

where T is transmittance, α is the absorption coefficient , d is the thickness of the sample. From the absorption coefficient data ,extinction coefficient (K) can be calculated by :

$$K = \frac{\alpha\lambda}{4\pi} \quad \text{……..(2)}$$

The refractive index (n) can be calculated using the following relation[6]:

$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2} \quad \text{……..(3)}$$

The calculated value of refractive index versus wavelength (λ)is shown in Figure(2) . The optical properties of solids are usually described in terms of the complex dielectric function $\varepsilon(E)=\varepsilon_1(E)+i\varepsilon_2(E)$ .The real part ε_1 and the imaginary part ε_2 of this description are both frequency dependent quantities , which include all desired response information . The quantity ε_2 is thought to contain many useful physical information about the material ,it is well known that ε_2 is considered to be superimposed from many independent contributions by interband transitions at energies E>> Eg , interband transition near the absorption edge , free carrier absorption and by optical phonon absorption .Namely there are four terms that contribute to the real part of dielectric constant .In transparent region ,K has very small value and is negligible and therefore all above terms result in the normal dispersion [7]. According to the single oscillator model, the only contribution to the dispersion of dielectric constant is due to interband transition and assumed that each electron behave as an oscillator [8].So the dielectric constant (ε_1) can be given as:

$$\varepsilon_1(\omega) = 1 + \frac{F}{E_o^2 - (h\omega)^2} \quad \text{….. (4)}$$

In this single-oscillator approximation , E_o and F are parameters dependent on electric dipole oscillator .In Wemple – DiDomenic model (WDD) ,the parameter F is expressed as $F=E_dE_o$, E_d is defined as dispersion energy and E_o as a single –oscillator energy .Finally ,the dielectric constant for any material can be given by [9]:

$$\varepsilon_1(\omega) = n^2(\omega) - 1 = \frac{E_o E_d}{E_o - (h\omega)^2} = \frac{E_d}{E_o}[1 - \frac{(h\omega)^2}{E_o^2}]^{-1} \quad \text{...(5)}$$

The dispersion energy E_d is the measure of the strength of interband optical transition and

can be considered as a parameter having very close relation with the charge distribution within unit cell and therefore with the chemical bonding .The other dispersion parameter , E_o , is usually considered as an " average" energy gap (E_g^{WDD}) and is empirically related to the lowest direct Tuac energy gap (E_g^T) .The dispersion parameters E_o and E_d are described by means of the r[th] moment of the $\varepsilon_2(E)$ optical spectrum .It is known that the r[th] moment of $\varepsilon_{2\,(E)}$ spectrum is defined as [8,9] :

$$M_r = \frac{2}{\pi}\int_{E_t}^{\infty} E^r \varepsilon_2(E)dE \quad \ldots(6)$$

where E=hω and E_t is the absorption threshold energy . One can develop some relationships between the dispersion parameters and $\varepsilon_{2(\omega)}$ spectrum via :

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \quad \ldots\ldots\ldots\ldots(7)$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \quad \ldots\ldots\ldots\ldots\ldots(8)$$

Where M_{-1},M_{-3} are moment of optical spectrum and the -1 , -3 moment are involved in computation of E_o and E_d .It is known that static dielectric constant of any substance is defined as:

$$\varepsilon_r(o) = \lim_{E \to o} n^2(E) = n_o^2 \quad \ldots\ldots\ldots(9)$$

The static dielectric constant can be written in term of dispersion parameters simply as :

$$n_o^2 = \varepsilon_r(o) = 1 + \frac{E_d}{E_o} \quad \ldots\ldots\ldots\ldots(10)$$

By plotting $(n^2-1)^{-1}$ against $(h\nu)^2$ and fitting a straight line as shown in Figure(3) , E_o and E_d are determined directly from the gradient $(E_oE_d)^{-1}$ and the intercept (E_o / E_d) on the vertical axis .The value of E_o , E_d , M_{-1} ,M_{-3} , $n_{(o)}$ and $\varepsilon_{(\infty)}$ are listed in table (I) .

E_o is interpreted as a measure of a separation between the centers of valance and the conduction bands , the calculated value of E_g^{WDD} by Wemple-Didomenico approximation is listed in table (II) .

Table(I):The estimated values of the oscillator parameters of (PVA-g-Ei)thin film .

E_o(eV)	E_d(eV)	n(o)	ε_∞	M_{-1}	M_{-3}(eV)$^{-2}$
2.073	3.35	4.12	2.03	1.615	0.379

According to Wagner et al. [10]the Muller rule is very convenient for visible and nonliner and near infrared frequancies,which equalize the third order nonliner polarizability parameter ($\chi^{(3)}$) through the equation[10]:

$$\chi^{(3)} = A(\chi^{(1)})^4 = A[E_oE_d / 4\pi(E_o^2 - (h\nu)^2]^4 = \frac{A}{(4\pi)^4(n^2-1)^4} \quad \ldots\ldots.(11)$$

where A =1.7x10^{-10} .

The third order nonlinear optical susceptibility of (PVA-g-Ei) thin film is calculated from equation (11) which is shown in Figure (4) . The most direct and perhaps simplest method for probing the band structure of semiconducting materials is to measure it's optical absorption spectrum , by studying the change in the transmitted optical intensity as a function of wavelength , one can investigate some possible quantum mechanical transition that the semiconductor electrons can make and learn much about the distribution of allowed electronic energy levels [11].In the strong absorption region (there is linear increase in α with increasing incident photon energy) , the relationship between the absorption coefficient and the photon energy is given by Tauc relation [1-12] :

$$\alpha h\nu = B(h\nu - E_g^T)^r \quad \ldots\ldots\ldots(12)$$

where B is constant, E_g^T is Tauc energy gap , r is the index that characterizes the absorption process . In (PVA-g-Ei) thin solid film analysis of experimental results showed that for r=1/2 .plot of $(\alpha h\nu)^{1/r}$ against hν shows one linear relation is most fitted for equation (12) , this indicates that the allowed direct transition is responsible for interband transition in (PVA-g-Ei) thin film , the value of E_g^T is obtained by plotting $(\alpha h\nu)^2$ against (hν) in Figure(5) followed by extrapolating the linear region of the plot (αhν) =0 ,the optical Tauc band gap for

(PVA-g-Ei) thin film, we can also calculate the direct energy gap (E_g^A) by absorption spectrum which was about (2.08eV) as shown insert Figure(12) [13].All data are listed in table (II).It is well known that electronic transport properties of organic semiconducting polymers depends on their chemical structure[14] , because E_g depends upon the molecular structure of the repeat unit ,it is clear from chemical structure Figure(1) of the compound that there are many π-electrons in the structure due to the aromatic groups , in such a structure large numbers of electrons cause a decrease of excitation energy of the π-electrons .The π-band is divided into π and π^* ,since each band can hold two electrons per atom (spin up and spin down) ,the π-band is filled and the π^* band is empty ,the energy difference between the height occupied state in π-band and the lowest unoccupied state in the π^*-band is the π-π^* energy gap (E_g) .Quite commonly in direct gap semiconducduing materials , disorder due to impurity and temperature effect will cause exponential band tails of electronic states to extend into the forbidden gap .Then near the absorption edge ,optical transitions from a parabolic band to an exponential band-tail states are manifested by an exponentially varying absorption coefficient [15,16] ,the absorption coefficient then is given by :

$$\alpha = \alpha_o e^{\frac{h\nu}{E_u}} \qquad \text{…..(13)}$$

E_u is Urbach energy corresponding to the width of the band tails . Figure(6) represents the linear dependence of (ln α) with photon energy (hν) for investigating (PVA-g-Ei) thin film , the slope of the line gives the magnitude of E_u which listed in table (II) . It is known that unsaturated bond are responsible for the formation of some defects in the film , such defects produce localized states or tail states in the forbidden gap of amorphous solids .The presence of high concentration of localized states in the band structure is responsible for the low value of the optical gap (E_g) . Photoluminescence (PL) is the spontaneity of light from a material under optical excitation ,the excitation energy and intensity are chosen to probe different regions and excitation concentrations in the sample .When light of sufficient energy is incident on a material, photons are absorped and electronic excitations are created.If radiative relaxation occurs , the emitted light is called PL .This light can be collected and analyzed to yield a wealth of information about the photoexcited material. The PL spectrum provides the transition energy ,which can be used to determine electronic energy level .The PL intensity gives a measure of the relative rates of radiative and non-radiative recombination .Variation of the PL intensity with external parameters like temperature and applied voltage can be used to characterize further the underlying electronic states and bands . PL investigation can be used to characterize a variety of material parameters . PL spectroscopy is a selective and extremely sensitive probe of discrete electronic states. Features of the emission spectrum can be used to identify surface ,interface and impurity levels and to gauge disorder and interface roughness.The fundamental limitation of PL analysis is its reliance on radiative events. Material with poor radiative efficiency ,such as low-quality indirect band gap semiconductors ,are difficult to study via ordinary PL . Similarly, identification of impurity and defect states depends on their optical activity .Although PL is a very sensitive probe of radiative levels, one must rely on secondary evidence to study states that couple weakly with light[17].Figure(7) illustrates the fluorescence spectrum of (PVA-g-Ei) thin film , the figure illustrates a strong absorption peak occurred in emission wavelength about 643nm related to eosin dye moieties , also from figure(7) the photoluminescence energy gap (E_g^{PL}) was estimated to be about 1.92eV .The value of the quantum yield (Φ_{PL}) parameter indicated that these materials are promising as light emitting diode(LED) applications[15] . Quantum yield (Φ_{PL}) is related to intensity of emission and excitation photons according to the relation [18]:

$$\Phi_{PL} = \frac{photons_{EM}}{Photons_{Abs}} \qquad \text{…..(14)}$$

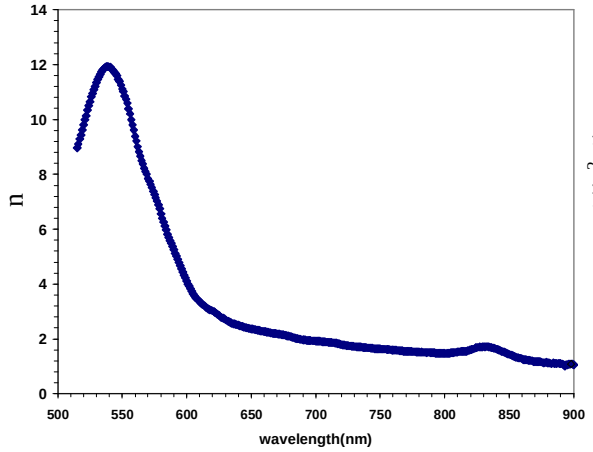
The calculated value of (Φ_{PL}) is 0.84, this result indicates that the polymer can be used as active layer in organic light emitting diodes applications. The calculated values of energy gap ,Urbach tail energy and the quantum yield are listed in table(II) .

Table(II): The calculated values of energy gap , by Wemple-DiDomenico approximation, by Tauc relation , absorption spectrum and by photoluminescence measurements respectively , also the calculated values of Urbach tails energy and the quantum yield (Φ_{PL}) .

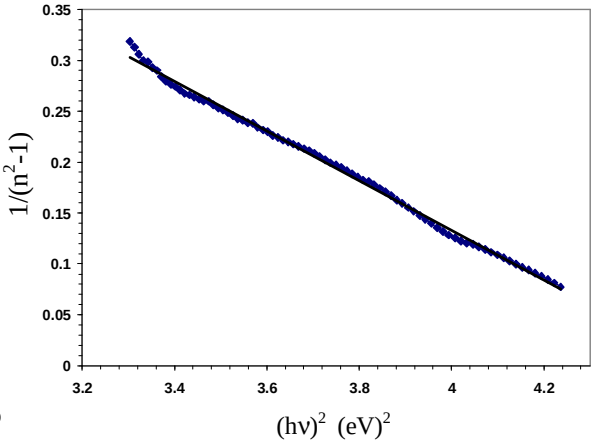
$E_g^{WDD}(eV)$	$E_g^{T}(eV)$	$E_g^{PL}(eV)$	E_u (meV)	$E_g^{A}(eV)$	Φ_{PL}
2.073	2.08	1.92	244	2.08	0.84

Conclusions:

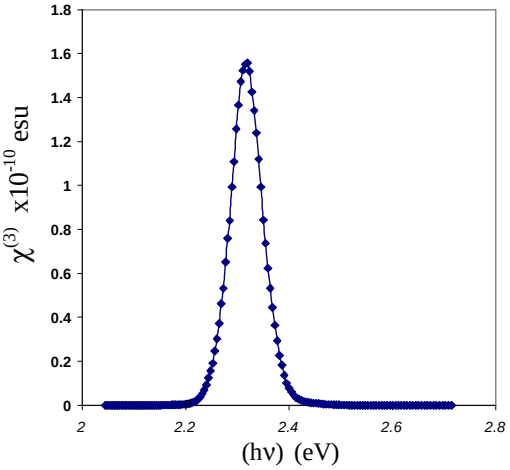
PVA-g-Ei thin films have been prepared by cast method technique, the dispersion of the refractive index in the film follows the single oscillator model . Using this method the values of the oscillator parameters were obtained ,the value of the direct energy gap (E_g^{WDD}) was calculated using Wemple-DiDomenico approximation , the value of the third order nonlinear optical susceptibility was estimated using Miller's rule . The optical band is discussed using absorption spectrum ,direct energy gap were calculated by using different methods such as Tauc's relation(E_g^{T}),Absorption spectrum (E_g^{A}), localized tail states were also discussed and Urbach energy was calculated using absorption spectrum . Photoluminescence measurements were used to calculate the energy gap (E_g^{PL}) and the quantum yield (Φ_{PL}) . The calculated values of energy gap by different approaches listed in table(II) for E_g^{WDD} , E_g^{T} , E_g^{A} and E_g^{PL} were roughly the same . The value of nonlinear optical susceptibility ($\chi^{(3)}$) indicated that new polymer can be used widely in many photonic electronic applications .



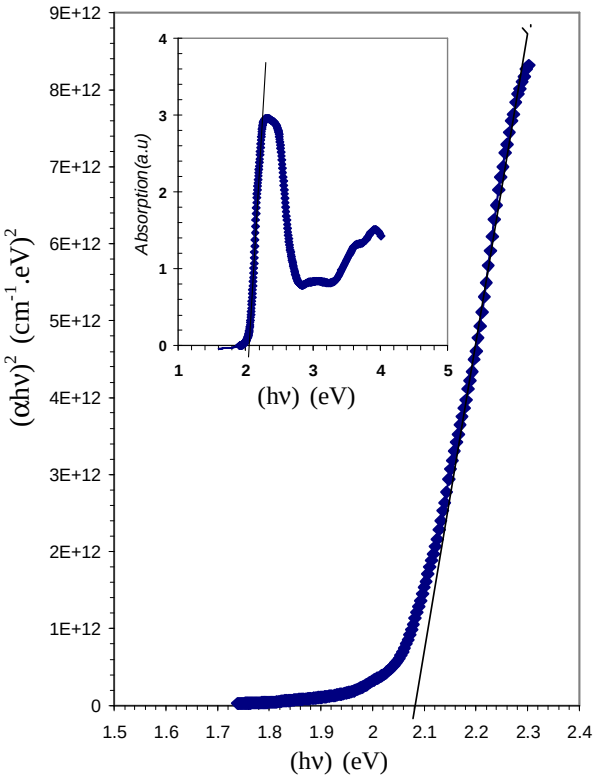
Figure(2)The relationship between reflective index and wavelength for (PVA-g-Ei) thin film



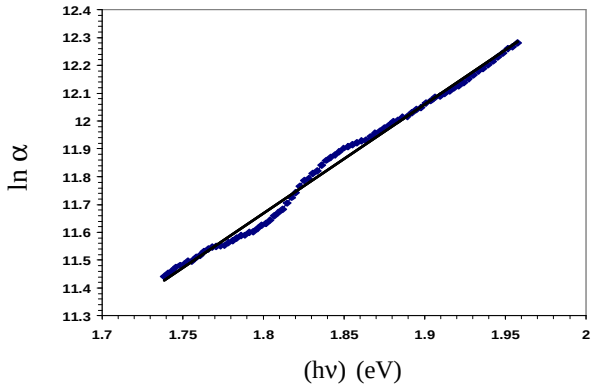
Figure(3):The relationship between $1/(n^2-1)$ and $(hv)^2$ for(PVA-g-Ei) thin film



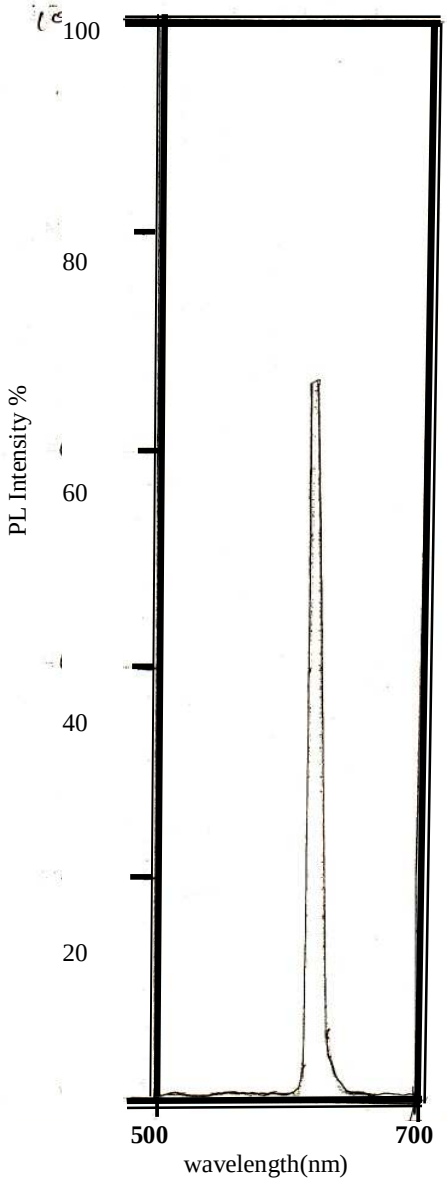
Figure(4):The relationship the third order nonlinear optical susceptibility and photon energy for (PVA-g-Ei) thin film



Figure(5):The relationship between $(\alpha h\nu)^2$ and photon energy for(PVA-g-Ei) thin film. Insert the relationship between absorption and wavelength



Figure(6):The relationship between ln α and photon energy for(PVA-g-Ei) thin film



Figure(7): Fluorescence spectrum for (PVA-g-Ei) thin film

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الملخص:

تم دراسة الخصائص البصرية للغشاء البوليمري بولي الكحول الفاينيل المطعم بصبغة الايوسين المرسب بطريقة الصب عند مدى الاطوال الموجية (200–900)نانومتر .معاملات التفريق لمعامل الانكسار اعتمدت على نموذج ويمبل – ديدمينكو احادي الطاقة . العديد من البارمترات تم حسابها حسب هدا النموذج مثل طاقة التدبدب الاحادية

(E_o) وطاقة التفريق(E_d) ومعامل الانكسار ($n_{(O)}$)وثابت العزل (($\varepsilon_{(\infty)}$) ومعاملات الزخم(M_{-1},M_{-3})

وفجوة الطاقة بطريقة ويمبل–ديدمينكو والتاثرية الضوئية اللاخطية($\chi^{(3)}$)التي نوقشت على ضوء قوانين ميلر .

تم حساب فجوة الطاقة من حافة الامتصاص الاساسية لطيف الامتصاص ومن علاقة تاوك ومباشرة من طيف الامتصاص , كما تم حساب طاقة مستويات الاقتناص يورباخ . تم تشخيص الاضاءة الفوتنية لغشاء رقيق من البولي الكحول الفاينيل المطعم لصبغة ناتج الكم للاضاءة الفوتنية(Φ_{PL}) وفجوة الطاقة (E_g^{PL}) الايوسين لمدى للاطوال الموجية (500–700)نانومتر .