

The MR affect on optical properties for poly (Vinyl alcohol) films

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Abstract :

optical properties of pure poly(vinyl Alcohol) films and poly(vinyl Alcohol) doped with methyl red were study, different percentage prepared with constant thickness using casting technique. Absorption, Transmission spectra have been recorded in order to study the optical parameters such as absorption coefficient, energy gap, refractive index, Extinction coefficient and dispersion parameters were measured in the wavelength range (200-800)nm. This study reveals that the optical properties of PVA affect by increasing the impurity concentration.

Key words: PVA polymers, Red methyl, optical properties, dispersion parameters.

Introduction :

Polymeric materials have attracted the scientific and technological researchers, because of their wide applications. This is mainly due to the lightweight, good mechanical strength, optical properties and makes them to be multifunctional materials. Moreover, these polymers are traditionally considered as an excellent host material for composites. Poly(vinyl alcohol) (PVA) is a polymer that has been studied intensively due to its several interesting physical properties, which are useful in technical applications including biochemical and medical [1]. And is of relatively low cost in manufacture [2]. In recent years, the doped polymers have been the subjects of interest for both theoretical and experimental studies, because of the physical and chemical properties needed for specific application may be obtained by adding or doping with some dopant [1].

Recently, used ammonium dichromate doped PVA thin films to studied the refractive index and Transmissions of the doped films have been measured [3] also Studies the polythermal of electrophysical characteristic as functions of temperature for poly (vinyl alcohol) films doped with ammonium metavanadate or polyoxometalate [4] As well as the electrical properties of poly (Vinyl alcohol) with sodium fluoride (NaF) polymer electrolytes for electrochemical cell applications have been studied [5].

The purpose of the current investigation was to study the effect variation of percentages of methyl red (MR) on the optical properties of PVA films.

Material and Methods :

In this work the poly(vinyl alcohol) (PVA) used were obtained as a powder form (BDH chemicals) with

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molecular weight (10000g/mol). The PVA films with different weight of methyl red (MR) mixed were prepared by dissolving PVA and MR in distilled water and with stirring the solution by using magnetic stirrer for about (one hour) at (80 °C) for complete dissolution.

The solution was poured in to a cleaned glass plate (petradish) and kept till dried (24 hours) at (30 °C), the thickness of the produced films was constant.

Using UV-Visible spectrophotometer industrialize from (shimadzu UV-1601 PC) for optical studies of the PVA, with and without MR doped films. The absorption and transmission spectra, absorption coefficient (α), energy gap (E_g), refractive index (n), extinction coefficient (k), dispersion parameters was measured at normal incidence in the spectral rang (200-800) nm.

Results and Discussion :

Changes in absorption are reported as a function of wavelength. Fig (1) show the absorption spectra of the PVA (a-d) in the rang (200-800) nm. observed high absorption values in the short wavelengths but it was decreased with high wavelengths, while in the pure PVA sample the absorption decrease in the region (214–246) nm and hence slight change occurs in the beyond wavelengths. The presence of MR in the PVA samples showed a significant change in the absorption where observed a decrease of the absorption in the region (202–240) nm for sample (b), (202-242) nm for sample (c) and (208–244) nm for sample (d) and a new peak at wavelengths (428,422,424) for samples (b,c,d) respectively for different concentration, slight change occurs absorption in the high wavelengths. Increase MR concentration was accompanied increase in absorption for all samples.

The formation of new peaks for samples (b,c,d) and broadening of those peaks with increasing MR is an indication of change in the molecular structure (degradation, polymer fragments, or free radicals) of PVA and/or PVA /MR film samples by exposure [6].

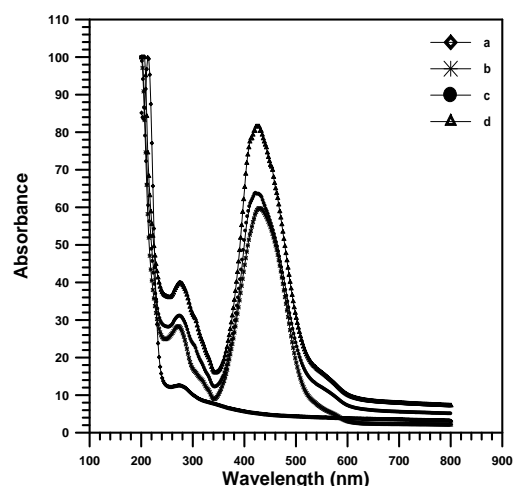


Fig (1): The absorption spectra of PVA (a-d) films

Fig (2) shows the transmittance spectrum in the rang (200-800)nm, It is clear from this figure that transmittance spectra for all films increased with increasing wavelength, while it observed increased of the transmittance for pure PVA sample in the rang (214-256)nm and hence slight increase occurs in the larger wavelengths while (b, c, d) sample were increased of its transmittance in the rang (202-246)nm, (202-252)nm, (208-254)nm respectively.

The Transmittance changed after addition of MR in the PVA samples, it is transmission intensity decreases with increasing MR concentration and formation a new peak at wavelength (340, 344, 344)nm for samples (b,c,d) respectively, also broadening of those peaks with increasing MR, This indicates a considerable interaction between PVA and MR.

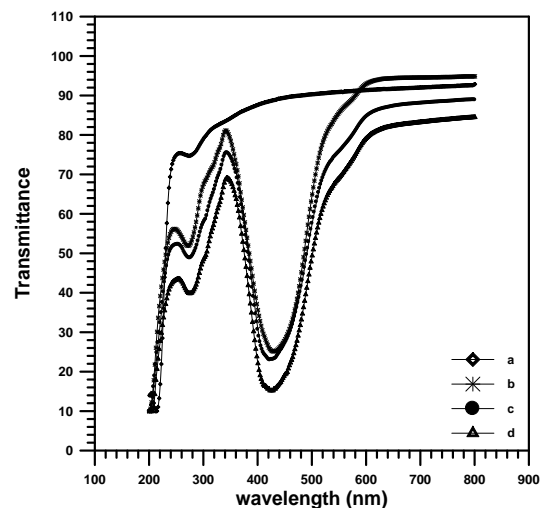


Fig (2): The transmission spectra of PVA (a-d) films

The optical absorption coefficient(α) of PVA films is very important because it provides information on the electronic band structure, the band tail and energy gap [7].

We used the following equation to determine the absorption coefficient [8]:-

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

where: A is the absorbance, d is the film thickness.

Fig (3) shows the dependence of the absorption coefficient on the photon energy for samples pure and samples with different impurity percentage. For all PVA samples one can observe a slight increase up to approximately (5.16 eV) for sample pure (a) and (2.23 eV) for samples (b,c,d) which may be attributed to electronic transitions from the bonding molecular orbit to nonbonding molecular orbit. The marked increase of the absorption coefficient at higher energies may be attributed to extra transition from the bonding molecular orbit to nonbonding molecular orbit [7].

The observed increase of the absorption coefficient after exposure and with increase MR concentration of PVA films can be attributed to the existence of more transitions from higher vibration levels of the ground state to higher sublevels of the first excited singlet state [9].

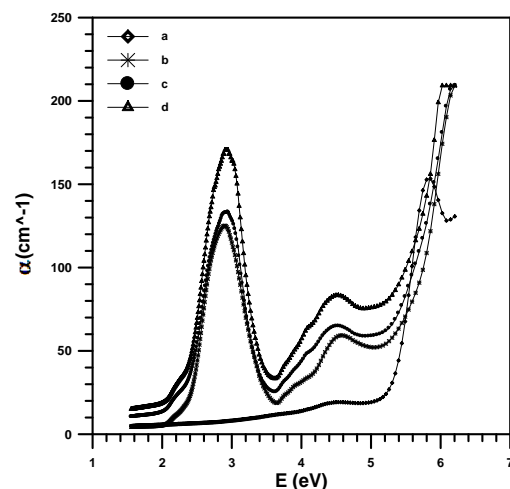


Fig (3): Variation the α as a function of E

The electronic transition between the valance and conduction transition of electron can be allowed as permitted by the transition probability (p) or forbidden. The transition probability is given by the equation:-

$$(\alpha h\nu)^p = A(h\nu - E_g) \dots\dots\dots(2)$$

Where E_g denotes the band gap, $h\nu$ the energy of the incident photon and A is a constant. The exponent p is a number which characterizes the transition and band gap E_g is suitable value of p [10]. The experimental data were fitted to the theoretical Eq (2) for different values of P and the best fit was obtained for $P=1/2$ this behavior indicated that the transitions are allowed indirect transitions.

The indirect allowed band gap was determined by plotting $(\alpha h\nu)^{1/2}$ as function of photon energy E for samples (a, b, c, d) as shown in figure (4), the graph is a straight line and the

value of E_g is obtained by extrapolating the linear portion of the graph to intercept the photon energy axis [10].

showing the values of indirect allowed gap are mentioned in table (1). These

values shows that the presence of MR lead to decrease in the optical energy gap for all samples according to the impurity concentration, figure (5).

Table (1): The optical properties of PVA samples (a-d).

samples	MR(wt%)	E_g (eV)	E_o (eV)	E_d (eV)	$S_o \cdot 10^{15}(\text{m}^{-2})$	$\lambda_o(\text{nm})$	$n(0)$	ϵ_{∞}	M_1	$M_3(\text{eV})^{-2}$
a	0	5.16	5.36	1.21	0.43	52647.76	1.10	1.22	0.22	0.007
b	1.4	5.14	3.10	2.09	0.71	69744.06	1.29	1.67	0.67	0.069
c	1.6	4.95	4.63	3.01	1.13	66574.79	1.65	2.72	0.65	0.030
d	1.8	5.12	4.81	4.70	1.99	58881.05	1.40	1.97	0.97	0.042

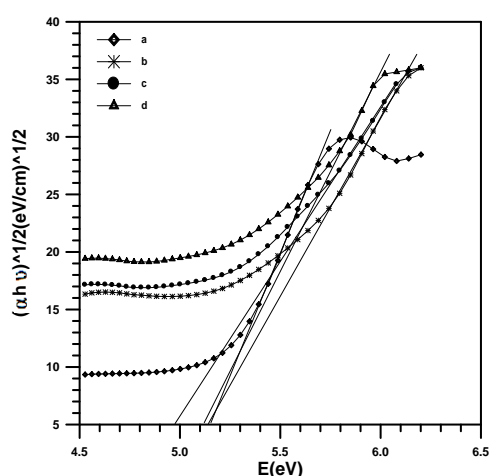


Fig (4): Variation the $(\alpha h\nu)^{1/2}$ as a function of E

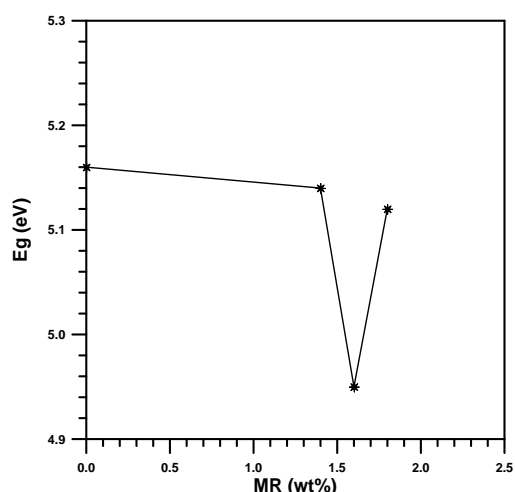


Fig (5): Variation the E_g as a function of MR (wt%)

The decrease in E_g with increasing MR concentration can be understood by considering the mobility gap variation in the doped polymer.

Also the decrements of (E_g) may be due to the transition between the molecular orbitals, which have highest occupied molecular orbitals instead of transition between valence–conduction band gap, polymers are usually amorphous insulators so one would consider the transition between the highest occupied molecular orbital and the lowest unoccupied molecular orbital instead of a valence–conduction band gap [6].

Also This decrease in band gap may be attributed to the presence of unstructured defects, which increase the density of localized states in the band gap and consequently decrease the energy gap [11].

The refractive index (n) is a fundamental optical property of polymers that is directly related to other optical, electrical and magnetic properties, and also of interest to those studying the physical, chemical, and molecular properties of polymers by optical techniques [12].

The refractive index of the films has been determined from the transmittance T , the variation of refractive index of the PVA samples (a-d) films of pure and different impurity percentage with the wavelength of the incident photon is shown in figure (6), high refractive index was observed in the short

wavelengths and hence decrease occurs in the high wavelength.

The refractive index of PVA films is found to increase after exposure of MR as well as increasing with increase MR concentration. The polymers with high refractive index are very useful in optics and photonics due to their ability to reduce reflection losses at interfaces and, hence, increase light output [13].

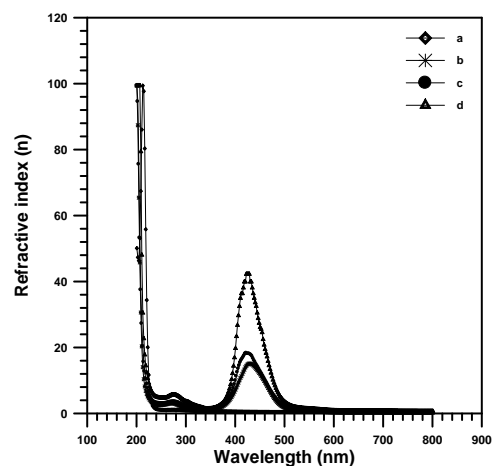


Fig (6): Variation the n as a function of wavelength

The (n) depends on the strength of the bonds, on density, and on molecular weight [14]. All the samples after exposure showed tow bands at the same positions (274)nm for samples (a,c,d) and (272)nm for sample (b) of the first band but showed an bands shifted to behind for second bands (428, 422,426)nm for samples (b,c,d) respectively with increased wavelength as the impurity percentage increased, which indicates that the samples have the no same structure. Hence, the change in the doped percentage gave change in the chemical composition of the polymer [2].

Figure (7) represent the dependence of extinction coefficient (k) on the wavelength of the incident photon. It is observed that the extinction coefficient of PVA samples (a-d) is found to decrease with

increase wavelength. The high extinction coefficient values of the short wavelengths were happened because the lose in incident wave energy because the operational absorption but the few extinction coefficient values of the high wavelengths was happened because the increase coating transmittance magnitude for this coating region for films [15]. extinction coefficient was increased for PVA films after exposure and with increase impurity concentration because the increase in absorption coefficient (α) where the extinction coefficient depending on absorption coefficient by the equation [8,15] :

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

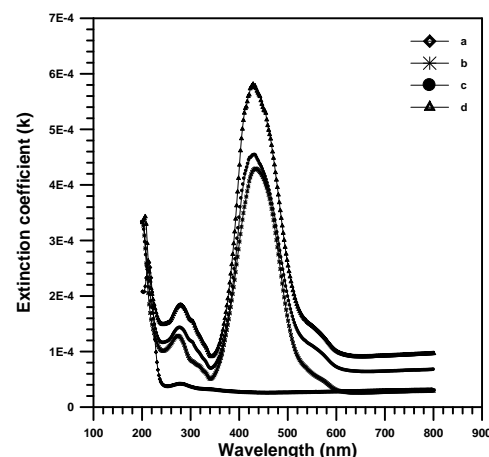


Fig (7): Variation the k as a function of wavelength

Wemple and Didomenico was proposed the dispersion in the refractive index can be filled the single oscillator model, the refractive index dispersion data were according to this model is then using the following relation [16] :-

$$n^2-1 = \frac{E_o E_d}{E_o^2 - (h\nu)^2} \dots\dots\dots(4)$$

Where E_o is the single oscillator energy parameter and E_d is the

dispersion energy which is a measure of the strength of the interband transitions.

Dispersion parameters E_o and E_d can be calculated by a plot of $(n^2-1)^{-1}$ versus E^2 as shown in figure (8).

The static refractive index $n(0)$ evaluated from equation (4) then the value of static dielectric constant ϵ_∞ was Calculated. The E_o , E_d , $n(0)$, ϵ_∞ values as mentioned in table (1).

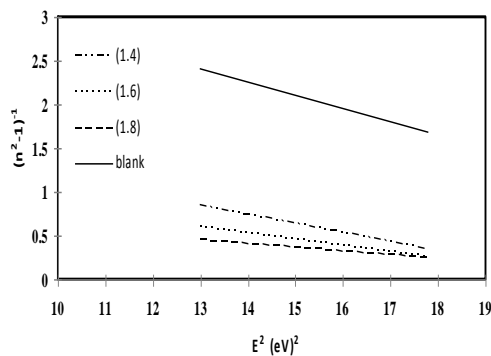


Fig (8): Variation the $(n^2-1)^{-1}$ as a function of E^2

The refractive index (n) dependence on the light wavelength by the following equation used :-

$$n^2(\lambda)-1 = \frac{S_o \lambda_o^2}{1 - (\lambda_o/\lambda)^2} \dots\dots(5)$$

where: λ_o is the average oscillator position and S_o is the average oscillator strength .

The parameters S_o and λ_o is calculated by the draw plotting $(n^2-1)^{-1}$ versus λ^{-2} , show is fig (9). The S_o , λ_o values as mentioned in table (1).

According to the single oscillator model, the single oscillator parameters E_o and E_d are related to the moments of the imaginary part of the optical spectrum. the M_{-1} and M_{-3} moments can be derived from the following relations and are given in table (1) [11]:-

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \dots\dots\dots(6)$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \dots\dots\dots(7)$$

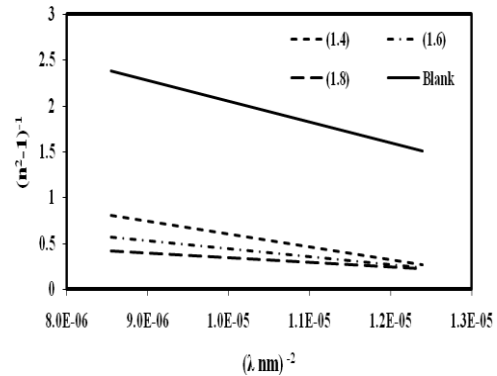


Fig (9): Variation the $(n^2-1)^{-1}$ as a function of λ^{-2}

Conclusion :

The detailed study of MR concentration effect on:

- 1- the Absorption, absorption coefficient, refractive index and Extinction coefficient were increased while the Transmission decrease as MR concentration increased.
- 2- The presence of MR lead to increase the density of localized states in the band gap and consequently decrease the energy gap.
- 3- The dispersion energy, static refractive index, static dielectric constant, average oscillator position, average oscillator strength, the imaginary part of the optical spectrum M_{-1} and M_{-3} were increases while the single oscillator energy parameter were decreased.

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تأثير إضافة المثل الأحمر على الخصائص البصرية لأغشية بولي فينايل الكحول

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الخلاصة :

في هذا البحث تم دراسة الخصائص البصرية لأغشية بولي فينايل الكحول (PVA) النقية والمشوبة بالمثل الأحمر (MR) بنسب مختلفة بعد تحضيرها بسمك ثابت باستخدام طريقة الصب. قيس كل من طيفي الامتصاصية، النفاذية، بالإضافة الى المعلمات البصرية المتمثلة بمعامل الامتصاص، فجوة الطاقة، معامل الانكسار، معامل الخمود، معلمات التفريق، لمدى من الأطوال الموجية (200-800nm). من خلال هذه الدراسة تم التوصل الى ان الخصائص البصرية للبوليمر تتأثر بزيادة تركيز الشوائب.