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Evolution of the optical properties of PVA films filled with Sodium Iodide

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Abstract

Transparent films of polyvinyl alcohol with different doping Sodium Iodide concentrations were prepared by using solution cast technique. The optical absorption measurements were carried out for all samples at room temperature across the wavelength regions. The study has been also extended to include the changes in the optical parameters including the band tail width and band gap energies for the samples; It was found that the optical absorption is due to direct and indirect transitions, and the optical energy gaps values shifted to lower energies on sodium iodide concentration for all transitions. Also absorption spectrums after annealing for three hours at temperature 80^oC are investigated. Moreover, the study of complex refractive index showed dependence on dopant concentrations.

Key words: optical absorption, filler, extinction coefficient, annealing.

Introduction:

Polymer based materials provide a variety of interesting and new properties, which have attracted materials science and technological researchers, because of wide range of applications in various fields. This is mainly due to their salient features such as low cost, ease of handling, high environment stability, electrical, optical and mechanical properties. They have been chosen as a host matrix material. Doping of metal salts to organic polymer modifies its properties needed to a particular application in modern engineering [1].

In many technical applications, the observation of change in polymer structure is very essential. Optical and electrical studies constitute the most convenient and sensitive methods for studying the polymer structure [2-5]. These are influenced not only by the structure and nature of the dopant but also by the doping concentration and preparation methods [6].

The optical study is very interesting because it provides an important information about the absorbance, transmittance and reflectance of the observed polymeric films [7]. The optical absorption and especially the absorption edge present a useful method for the investigation of optically induced transition and for getting information about the band structure, the band tail and the energy gap of the polymeric materials under consideration [8].

This paper deals with investigations the effect of sodium iodide dopant concentration on optical properties of PVA films before and after annealing. The major aim of this study is to obtain a wide range of the physical properties of PVA films filled with different concentrations of sodium iodide in order to select the optimum conditions necessary for the required technical applications.

Optical Properties:

The importance of the absorption coefficient is related to the valuable information that can be obtained such as the electronic band structure and the optical energy band gap. The absorption coefficient $\alpha(\nu)$ can be estimated from the optical absorption spectrum owing to the following equation [9].

$$\alpha(\nu) = 2.303\frac{A}{d} \quad \text{………(1)}$$

where d is the film thickness in cm and A is defined by $\log\left(I_o\frac{\square}{I}\right)$ where I_o and I are the intensities of the incident and transmitted beams respectively.

Concerning the optical transitions resulting from photons of energy $h\nu > E_g^{opt}$, the present optical data can be investigated according to the following relationship for the near edge optical absorption [10].

$$\alpha(\nu)h\nu = B\left(h\nu - E_g^{opt}\right)^r \quad \text{……(2)}$$

where α is the absorption coefficient, ν is the frequency, h is Planck's constant, B is a constant, E_g^{opt} is the optical energy band gap between the valence band and the conduction band and r is the power that characterizes the transition process. Specifically, r can take the values $\frac{1}{2},\frac{3}{2},2, an\square\ 3$ for transitions designated as direct allowed, direct forbidden, indirect allowed, and indirect forbidden respectively [8]. The determination of the value of optical energy band gap E_g^{opt} involves the plotting of $(\alpha h\nu)^{\frac{1}{r}}$ against $h\nu$.

On the other hand, for optical transitions caused by photons of energy $h\nu < E_g^{opt}$, the absorption of photons is related to the presence of localized tail states in the forbidden gap. The width of this tail, called Urbach tail, is an indicator of the defect levels in the forbidden band gap. The following relation was used to calculate the width of the Urbach tail [11]

$$\alpha(\nu) = \alpha_o \, exp\left(\frac{h\nu}{\Delta E_t}\right) \quad \text{…....(3)}$$

where α_o is a constant and ΔE_t is the Urbach energy tail. The exponential dependence of $\alpha(\nu)$ on the photon energy ($h\nu$) for the samples indicates that it obeys Urbach's formula [12].

The reflectance (R) has been found from values of transmission (T), and Absorbance (A), using the relationship:

$R + T + A = 1$ ………(4)

For normal reflectance, the refractive index can be determined from the relation:

$n = \frac{(1+\sqrt{R})}{(1-\sqrt{R})}$ …………(5)

The extinction coefficient is related to the absorption coefficient α by the relation:

$k = \frac{\alpha\lambda}{4\pi}$ ………..(6)

Where λ is the incident photon wavelength.

Experimental detail:

Films of PVA - sodium iodide composite were prepared by solution casting; $1\ gm$ of pure Polyvinyl alcohol PVA supplied from Sigma-Aldrich company has been dissolved in $20\ ml$ of distilled water to obtain a pure PVA film; the doping to $(10, 20, 30\ and\ 40\ wt.\%)$ were prepared by mixing amount of $0.1, 0.2, 0.3, and\ 0.4\ gm$ of sodium iodide into pure PVA solution, the complete dissolution was obtained using a magnetic stirrer at temperature 80^oC for $1hr$, these homogeneous solutions were spread on a glass plate. The whole assembly was plased in a dust free chamber and allowed to evaporate the solvent slowly in air at room temperature for $48h$. The thickness of the films was in the range of $(0.06 - 0.11)mm$, it was determined using micrometer at different places in each film and an average was taken.

Results and discussion:

Ultraviolet -Visible (UV/VIS) absorption spectra of the prepared samples were carried out at room temperature in the wavelength range $190 - 1100\ nm$ using a double beam Lambda-25 UV/VIS spectrophotometer. The spectrophotometer method was used to determine the optical constants of the samples. The variation of the optical absorption with wavelength λ for all the prepared films is shown in Fig(1).

The spectrum of pure PVA is characterized by an absorption edge at wavelength $277nm$. No absorption peaks are noticed at higher wavelengths. This absorption edge can be attributed for carbonyl groups conjugated with one ethylinic group [13]; this peak was disappeared in higher doped samples as shown in Fig(1), while a new absorption peak at nearly $365nm$ was appeared, which may be attribute to the interaction between NaI and conjugate bonds in PVA. Moreover, the figure indicates that NaI enhances the UV absorption of the PVA host especially below 250 nm. This indicates that NaI may be acts as an excellent ultraviolet shield for PVA host especially at high NaI content.

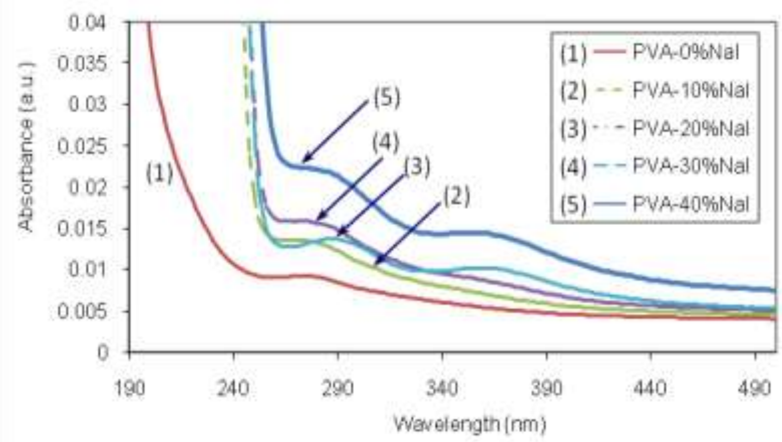
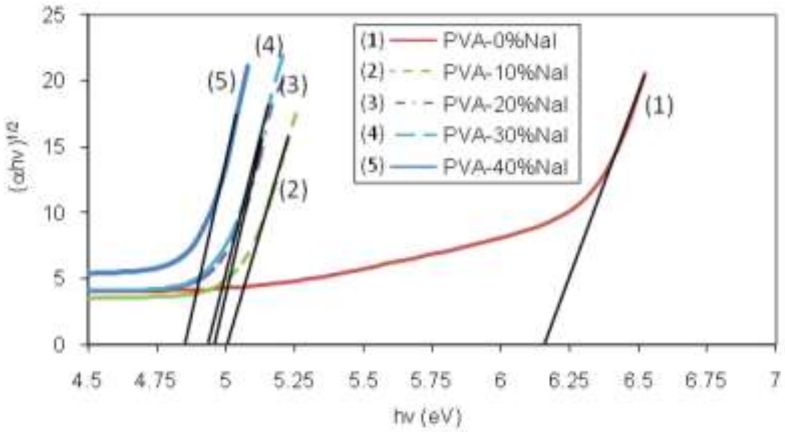


Fig (1): Optical absorption as a function of wavelength for PVA at different sodium iodide concentration.

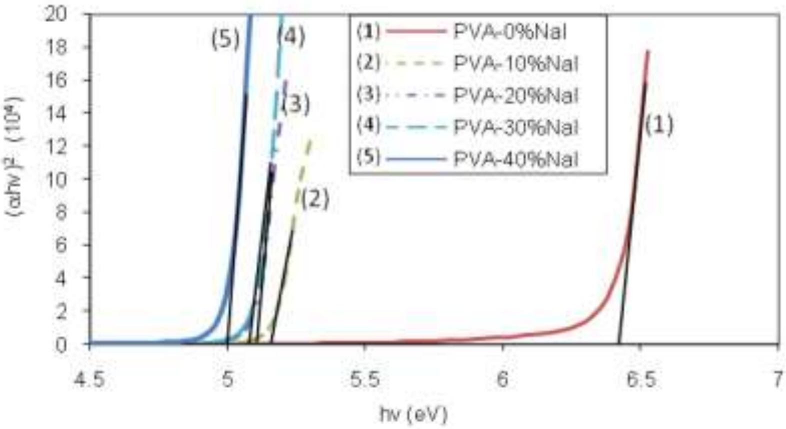
The plots of $(\alpha h\nu)^{\frac{1}{2}}$ versus $(h\nu)$ for the present experimental data near the absorption edge give a linear fit over a wide range of $h\nu$, Fig(2). This linearity suggests the presence of indirect allowed transitions in the investigated films filled with different contents of sodium iodide. Extrapolation of the linear portion of the plots to the abscissa yields the optical energy band gaps E_g^{opt} owing to the following equation.

$(\alpha h\nu)^{\frac{1}{2}} = B^{\frac{1}{2}}\left(h\nu - E_g^{opt}\right)$ …..(7)



Fig(2): Relation between the $(\alpha h\nu)^{\frac{1}{2}}$ and $h\nu$ for PVA with sodium iodide concentration.

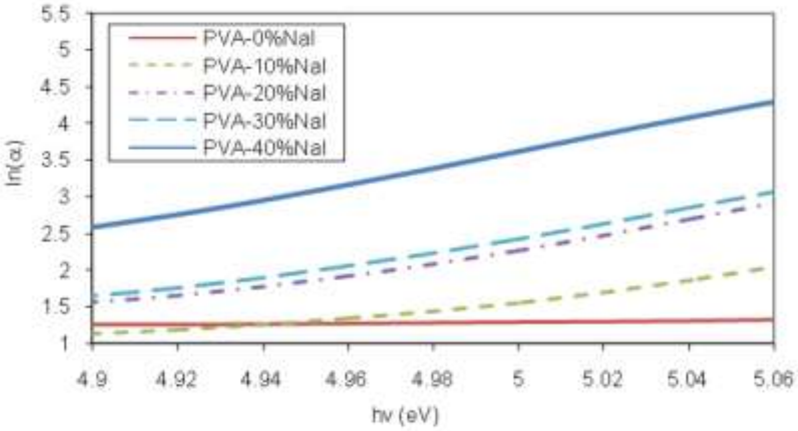
Fig (3) shows the dependence of $(\alpha h\nu)^2$ on the photon energy $(h\nu)$ for direct allowed transitions. It is to be noticed that the curve is characterized by the presence of an exponentially decaying tail at low photon energy. It is observed that the E_{opt} slightly decreased with increasing dopant concentration. All plots show straight lines with some deviations from linearity at the lower of α , which were suggested by Redfield and Afromowitz [14] as possibly due to imperfections in the material, but this region of the curve is still not fully understood.



Fig(3): Relation between the $(\alpha h\nu)^2$ and $h\nu$ for PVA with sodium iodide concentration.

The variation of the calculated values of the optical energy gap may reflect the role of sodium iodide in modifying the electronic structure of the PVA matrix due to appearance of various polaronic and defect levels [8]. The decrease in the optical energy band gap with filling may be explained on the basis of the fact that the incorporation of small amounts of dopant forms charge transfer complexes in the host matrix [2,5]. These charge transfer complexes increase the electrical conductivity by providing additional charges, this results in a decrease of the optical energy gap. As the dopant concentration is increased, the dopant molecules start bridging the gap separating the two localized states and lowering the potential barrier between them, thereby facilitating the transfer of charge carrier between two localized state [15].

In order to illustrate this dependence, the natural logarithm of the absorption coefficient $\alpha(\nu)$ was plotted as a function of the photon energy ($h\nu$) for the studied films, Fig(4). The magnitudes of the Urbach energy ΔE_t were estimated by taking the reciprocal of the slopes of the linear portion of these curves. Noting that the origin of ΔE_t can be considered as thermal vibrations in the lattice [8].



Fig(4): Relation between the $ln(\alpha)$ and $h\nu$ for PVA at different sodium iodide concentration.

The present experimental results concerning the direct and indirect optical energy band gaps and the Urbach energy tail ΔE_t depict that filling significantly affects these optical absorption parameters.

The optical band gap and band tails of the localized state of the samples before and after annealing at temperature 80^oC for three hours, are tabulated in Table(1). The increase of the band gap of these films after thermal treatment, and the redaction of tail localized state to lower energy often gives rise to stability and relaxation of these organic molecules [16].

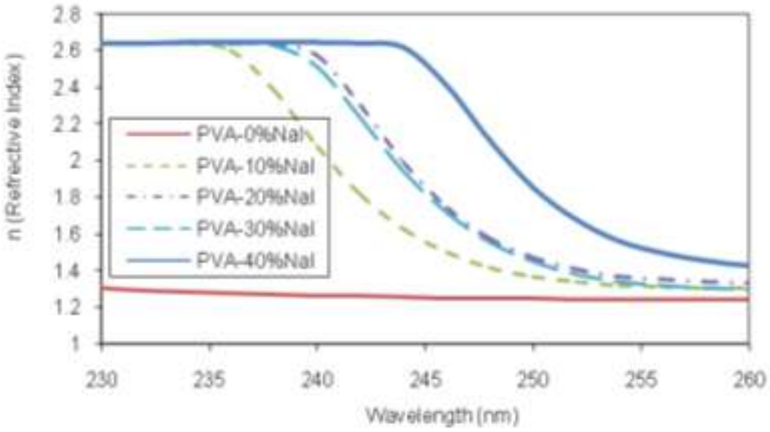
Since, the magnitudes of activation energies within the limits suggested by Jonscher for electronic conduction ($\leq 0.8\ eV$) [2], the dominant charge transport is through the motion of electrons both for pure and doped films.

Table(1): Direct, indirect optical energy gap, and band tail for PVA doped with sodium iodide, before and after annealing.

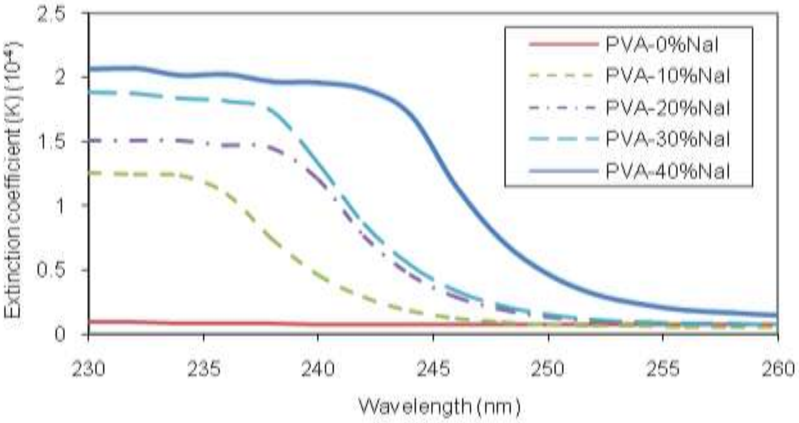
Samples	Before annealing			After annealing		
	Direct E_g^{opt} (eV)	Indirect E_g^{opt} (eV)	ΔE_t (eV)	Direct E_g^{opt} (eV)	Indirect E_g^{opt} (eV)	ΔE_t (eV)
$PVA - 0\%\ NaI$	6.41964	6.14923	0.17363	6.4255	6.15816	0.1726
$PVA - 10\%\ NaI$	5.1505	4.99745	0.1453	5.15433	5.0051	0.141894
$PVA - 20\%\ NaI$	5.099489	4.94898	0.12719	5.108418	4.9579	0.12484
$PVA - 30\%\ NaI$	5.07015	4.92857	0.11504	5.08673	4.932398	0.1146
$PVA - 40\%\ NaI$	4.99107	4.84438	0.0963	5.05102	4.895159	0.09491

The refractive index values have been calculated from a combination of reflectance and absorbance measurements at normal incidence. The variations of refractive index n of all films with wavelength in the exponential region was shown in Fig(5). For the same region, the extinction coefficient K over the exponential absorption region for all polymer samples were shown in Fig(6). It is clear from these figures, that the refractive indes n , and extinction coefficient K are decrease with increasing wavelength in the ultraviolet region; while they are fixed in the visible region.

In general the sodium iodide content in polymer matrix caused an increase of refractive index values, which is a result of increasing the number of atomic refractions due to the increase of the linear polarizability. The maximum value of refractive indices was at 2.63 for sodium iodide doping films.



Fig(5): Refractive index as a function of wavelength for PVA for different sodium iodide concentration.



Fig(6): Extinction coefficient K as a function of wavelength for PVA polymer with sodium iodide concentration.

Conclusions:

Polyvinyl alcohol films with different filling levels of sodium iodide have been prepared by solution cast method, and the optical absorption was performed. The optical energy band gap and the Urbach energy tail were evaluated and their dependence on filling was investigated. The decreasing trend of the optical band gap with sodium iodide concentration, which may be attributed to formation of charge transfer complexes, suggests the presence of the deeps localized state in the band gaps. The increase of band gap energy and the redaction of tail localized state of these films after thermal treatment were observed after thermal treatment.

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دراسة الخواص البصرية لأغشية PVA الممتلىء بصوديم الأيودين

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الملخص

تم في هذا البحث تحضير أغشية شفافة من البولي فينيل الكحول بتراكيز مختلفة لصوديوم الأيودين، بأستخدام طريقة الصب. و اجريت القياسات الأمتصاص البصري لجميع العينات في درجة حرارة الغرفة و ضمن الاطوال الموجية 190-1100 nm . و قد شملت الدراسة التغييرات في المعاملات البصرية و بما في ذلك عرض الذيل الحزمة و فجوة الطاقة لكافة العينات. و لقد وجد ان الامتصاص البصري ناتج عن الانتقالات المباشرة و الغير المباشرة، و ان القيم فجوة الطاقة تتغير الى الحدود الدنيا مع زيادة تراكيز صوديوم الأيودين و لكافة الانتقالات. وقد تم دراسة طيف الامتصاص بعد تلدين العينات بدرجة حرارة 80 ^{o}C و لمدة ٣ ساعات. اضافة الى ذلك أظهرت دراسة معامل الانكسار المعقد الأعتماد على تراكيز التشويب.