

Optical Characterization of Thin Films Poly (Ethylene Oxide) Doped with Cesium Iodide

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In this work, thin films of solid polymer electrolyte made of pure poly (ethylene oxide) doped with cesium iodide (CsI) were prepared using casting method. The films contain different (CsI) concentrations: 0 %, 1 %, 4 %, 8 %, 12 %, and 16 % by weight. The optical properties such as the absorption coefficient, energy gap, refractive index, extinction coefficient, and dielectric constants have been determined in the wavelength range (300 – 800) nm. The results obtained showed that the optical constants change with increase of cesium iodide concentration. The absorption spectra of thin films at different CsI concentrations showed changes in the wavelength range. The optical dispersion parameters have been analyzed by the single oscillator model. The value of E_o and E_d were found and the other parameters have been determined by Wemple-DiDomenico method.

Keywords: Polymer, Thin films, Cesium Iodide, Optical constants, Absorbance, Single oscillator model.

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1. INTRODUCTION

In recent years, optical properties of doped polymers thin films have been attracted considerable attention because of the range of technological applications that include solar cells, coatings, light emitting diodes, sensors and electrochemical cells. The attention of researchers has drawn to study effect of doping on the optical properties of solid polymer electrolytes be tailored to a specific requirement by the addition of suitable dopant substances.

The optical researches provide important informations about the absorbance, transmittance, reflectance, antireflection, and interference of the prepared polymeric thin films. Measurements and determination 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 [1, 2].

Knowledge of optical constants of solid polymer electrolytes (SPE) such as refractive index, optical gap and extinction coefficient is quite essential to examine material's potential opto-electronic applications. The optical properties of these materials can be tuned by controlling contents of the different concentrations [3]

The physical characterization of thin films of polymer electrolyte can be carried out using a variety of analytical technique, such as alternating current impedance, ultraviolet spectroscopy, in addition to direct current measurements. For example, Mohan et al [4] reported about the ionic conductivity for some PEO/salt electrolyte. Musa et al [5] studied thickness effect on the optical constants of Poly Methyl Methacrylate (PMMA) doped by Cesium Iodide via spectrophotometric measurements and analyzed the optical parameters by the single oscillator model. Ritu Tomar et al [6] studied microstructure, ionic conductivity, structural and mechanical properties of the Polyvinyl- pyrrolidone (PVP) / Potassium iodide polymer composite. They found that

the polymer conductivity of composite increases with the KI salt concentration where as tensile strength reduced. Manjeet Singh et al [7] reported new solid polymer electrolyte films of poly vinylpyrrolidone (PVP) complexed with Potassium iodide (KI). They reported that complex impedance spectroscopy reveals enhancement in electrical conductivity which reaches a maximum at 30 wt % CsI concentration. Al-Faleh and Zihlif [8] studied the optical absorption and constants of poly (ethylene oxide) (PEO) doped with sodium iodide NaI. They reported that the optical energy gap and the basic optical constants, refractive index, and dielectric constants of the PEO / NaI thin films have been affected by the NaI concentration. Recently, Al-Faleh et al. [9] reported about the electrical and thermal characterization of doped PEO polymer with sodium iodide, and found both the AC electrical and thermal conductivities increase with increasing temperature and NaI concentration. Also, they found that the percolation threshold of the AC conductivity occurs at about (1 wt. %) NaI dispersed in the PEO matrix.

In the present study, thin films of PEO doped with cesium iodide were prepared with different concentrations: 0 %, 1 %, 4 %, 8 %, 12 %, and 16 % by weight. Optical and dielectric constants of those films will be determined under different UV-radiation wavelengths and cesium iodide concentrations.

2. EXPERIMENTAL WORK

Casting method was used to prepare films of Poly (ethylene oxide) (PEO) with average molecular weight of 300,000 g/mol doped by dispersing particles of cesium iodide (CsI) at different concentrations. Solution was prepared by dissolving the PEO resin in acetone, and CsI was mixed as a dopant. The solution was stirred, by using a magnetic stirrer for 24 hours until the polymer completely dissolved. Then the solution was poured into flat glass plate dishes. Homogeneous solid films of the average thickness 70 μm were ob-

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tained after drying in air for 48 hours at room temperature. The composite films were dried in an oven at 42 °C for few days to remove any residual solvent. The optical absorption spectra of all films were recorded at room temperature, by UV-VIS (a Cary) spectrophotometer in the wavelength range 300-800 nm.

3. RESULTS AND DISCUSSION

Using the UV-visible spectrophotometer, the optical absorbance (A) spectra of the PEO / CsI thin films were collected at room temperature and in the wavelength range of 300 nm to 800 nm. The absorption coefficient $\alpha(\omega)$ was then calculated from the absorbance (A). After correction for reflection, $\alpha(\omega)$ was calculated using the following relation: $I = I_0 \exp(-\alpha x)$; Hence,

$$\alpha(\omega) \frac{2.303}{x} \log \left(\frac{I_0}{I} \right) = \frac{2.303}{x} A(\omega), \quad (1)$$

where x is the thin film thickness, and I_0 is incident intensity and I is transmitted intensity [10, 11]. The optical absorption spectra of all prepared films were recorded at room temperature, by UV-VIS (a Cary) spectrophotometer. The spectra in figure 1 show that increasing the CsI concentration, the absorbance decreases. The spectra also show that when the photon wavelength increases the absorbance decreases.

The optical energy band gap of crystalline and amorphous materials can be found by using the optical absorption spectrum. The fundamental absorption, which corresponds to the electron excitation from the valance band to the conduction band, can be used to determine the nature and value of the optical band gap [12]. We used this spectral range to find the position of optical absorption edge, and the effect of concentration of CsI dopant on the absorption edge and the value of optical energy gap.

From the linear part of the plots of $(\alpha \hbar \omega)^2$ against $(\hbar \omega)$ for the thin films, as shown in figure 2, the optical energy gap values have been determined according to Tauc formula [13]:

$$\alpha(\omega) \hbar \omega = \beta (\hbar \omega - E_g)^m \quad (2)$$

where $\alpha(\omega)$ is the absorption coefficient, β is an energy-independent constant, E_g is the optical band gap, the exponent m depends on the type of transition, where it is equal to 1/2 for direct, allowed transition. From the intercepts of extrapolations to zero with the photon energy axis $(\alpha \hbar \omega)^2 \rightarrow 0$, the values of E_g were determined. From the results obtained it is seen that increasing the concentration of CsI dispersed in the thin films leads to a decrease in the optical band gap value. The optical energy gap decreases from 2.13 eV (for pure PEO) to 1.96 eV at 16 % CsI concentration. The observed decrease in the energy band gap may be attributed to an increase in structural disorder of the polymer films [14]. The decrease in optical band gap on doping may be explained on the basis of the fact incorporation of small amounts of dopants forms Charge Transfer Complexes (CTCs) in the host lattice in addition of creation of ionic pathways [15]. The variation of optical band gap on doping is explained on the basis of

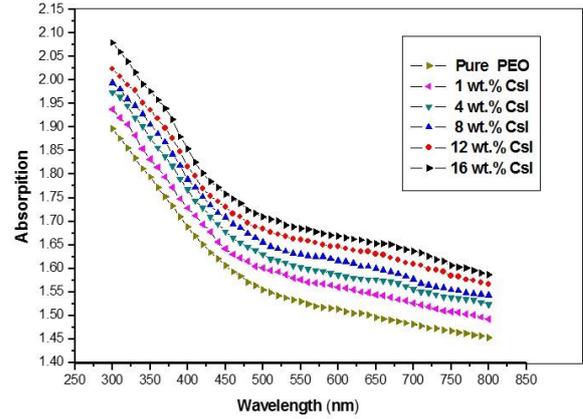


Fig. 1 – The optical absorption spectra of PEO/CsI thin films

incorporation of charge transfer complexes (CTCs) by the dopants. The absorption studies on thin electrolyte films have led to a variety of interesting optical phenomenon, which have thrown considerable light on the band structure of solids and phonic states.

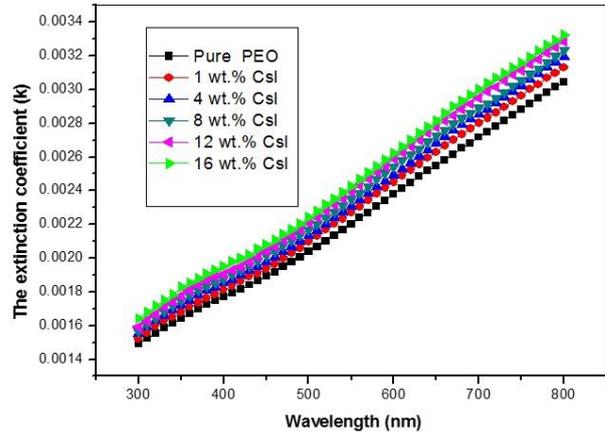


Fig. 2 – The plots of $(\alpha \hbar \omega)^2$ against $(\hbar \omega)$

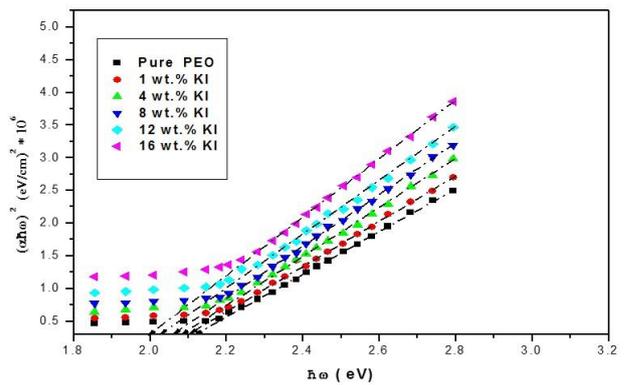


Fig. 3 – represents the Urbach plots for the prepared composite films

From the plots of $\ln(\alpha)$ against photon energy $(\hbar \omega)$ for these films, the optical Absorption edge values ΔE (eV) have been determined according to Urbach formula [16]:

$$\alpha(\omega) = \alpha_0 \exp(\hbar \omega / \Delta E) \quad (3)$$

where α_0 is a constant and ΔE is the energy gap tail interpreted as the width of the tails of localized states in the forbidden band gap. The extrapolated (ΔE) values listed in Table 1 were determined from the slope reciprocal of the linear part of each curve.

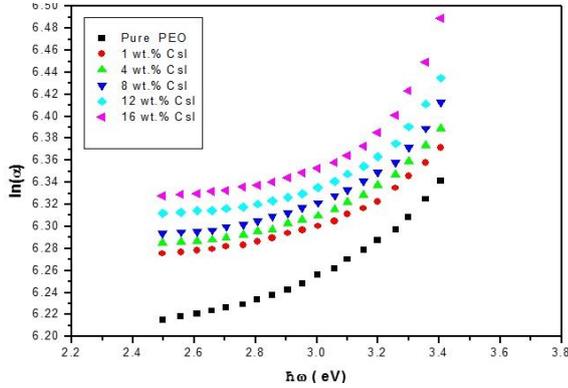


Fig. 4 – The plots of $\ln(\alpha)$ against photon energy ($\hbar\omega$)

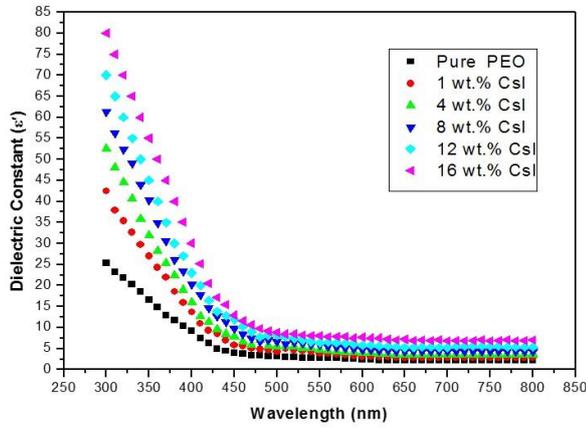


Fig. 5 – The variation of the refractive index (n) with UV-wavelength

The extinction coefficient (k) which is related to the absorption coefficient and the incident photon wavelength by:

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

The variation of the extinction coefficient (k) for the PEO/CsI with UV-wavelength is shown in figures 4. It shows that the extinction coefficient (k) increases with increasing the wavelength. Fig. 5 – shows the variation of the refractive index (n), which can be obtained from

the equation [17]:

$$n = \left\{ \left[\frac{4R}{(R-1)^2} - k^2 \right]^{1/2} - \frac{R+1}{R-1} \right\} \quad (5)$$

where (R) is the reflectance. The figure shows that the refractive index decreases rapidly at low wavelength (< 550 nm).

On the other hand, when the refractive index and the extinction coefficient are known, the real and the imaginary parts of dielectric constants of the composites can be calculated. The real and the imaginary parts of complex dielectric constant are expressed as:

$$\epsilon' = n^2 - k^2, \quad \epsilon'' = 2nk \quad (6)$$

the real part is associated with the term that shows how much it will slow down the speed of light in the material. The imaginary part shows how a dielectric absorbs energy from an applied electric field due to dipole motion. The variations of the real and imaginary components of the complex permittivity of the composites with the UV-wavelength are shown in figures 6 and 7, respectively [17]. The real and imaginary parts of the dielectric constant follow the same pattern curves but the values of the real part are higher than the values of the imaginary part [18].

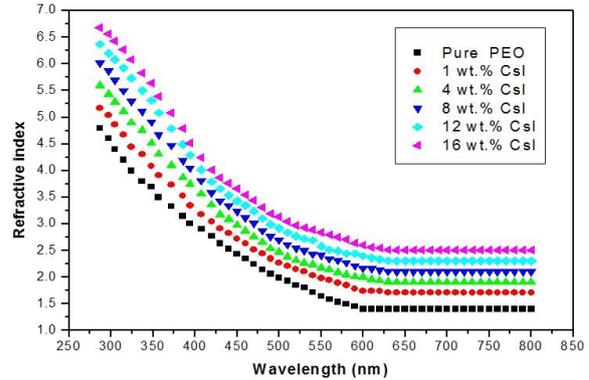


Fig. 6 – The variations of the real part of the complex permittivity with the UV-wavelength

The observed values of the refractive index of the doped polymeric thin films can be fitted by the Wemple–DiDomenico relationship [19]. The dispersion behavior below the interband absorption edge corresponds to the fundamental electronic excitation spectrum. Thus, the refractive index is related to photon

Table 1 – Optical values of PEO/CsI thin films

Thin films	Optical band gap E_g (eV)	Optical Absorption Edge ΔE (eV)	Single-oscillator energy parameter E_o	Dispersion energy parameter E_d
Pure PEO	2.13	0.52	3.24	5.04
1 wt.% CsI	2.11	0.69	3.27	6.23
4 wt.% CsI	2.08	0.91	3.29	9.96
8 wt.% CsI	2.06	1.37	3.31	15.76
12 wt.% CsI	2.03	2.11	3.35	23.58
16 wt.% CsI	1.96	2.86	3.42	31.09

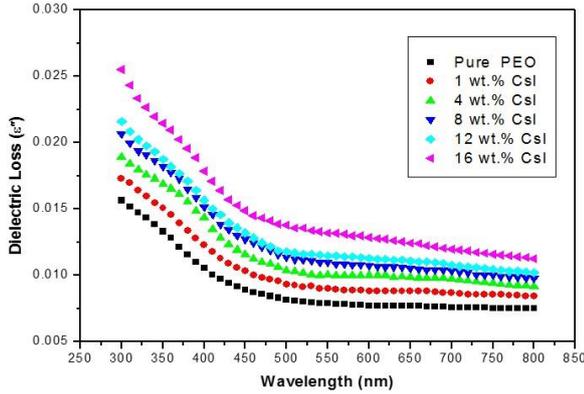


Fig. 7 – The variations of the imaginary part of the complex permittivity with the UV-wavelength

energy ($\hbar\omega$) through the relationship.

$$n^2 = 1 + \frac{E_0 E_d}{E_0^2 - (\hbar\omega)^2} \quad (7)$$

where E_0 and E_d are the single-oscillator energy and the dispersion energy parameter, respectively. The parameter E_d , which is a measure of the intensity of the inter-band optical transition, does not depend significantly on the band gap. The dispersion energy plays an important role in the researches of optical materials and it is a significant factor in optical communication and in designing devices for spectral dispersion. By plotting the values of $(n^2 - 1)^{-1}$ vs. $(\hbar\omega)^2$ for the PEO/CsI thin films, straight lines are obtained as shown in figure 8. E_0 and E_d can be determined directly from the gradient, $(n^2 - 1)^{-1}$ and the intercepts (E_0/E_d), on the vertical axis. E_0 and E_d values are included in table 1 which shows that E_d and E_0 values increase with increasing the dopant CsI concentration.

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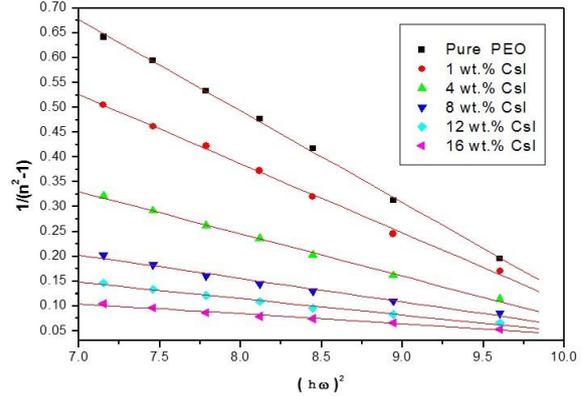


Fig. 8 – Plot of $(n^2-1)^{-1}$ vs. $(\hbar\omega)^2$ for the PEO/CsI thin films

4. CONCLUSIONS

In this study, the optical properties of the PEO/CsI thin films were prepared by casting and studied in the UV-wavelength range of 300 – 800 nm. The optical results and the photon energy obtained are analyzed in terms of the absorption formula for non-crystalline materials. The optical absorption edge (ΔE) increases with increasing CsI concentration, and the direct optical energy gaps show a decreasing trend with an increasing the dopant (CsI) concentration. The decrease in optical gap on doping may be explained on the basis of the fact that the incorporation of small amount of dopant forms charge transfer complexes (CTCs) in the host lattice. In addition of the formation ionic pathways and connections during the charges transport. The refractive index (n), real and imaginary parts of dielectric constants, and extinction coefficient were calculated. It was found that the refractive index and the dielectric constants increased with increase in the CsI concentrations. The dispersion energy and single-oscillator energy parameters were determined for the PEO/CsI thin films. These values increase with increase in the CsI concentrations.

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