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Analysis of the UV – Visible spectra of $KMnO_4$ doped PVA-PVP blend

Veena. G and Blaise Lobo*

Department of Physics, Karnatak University's Karnatak Science College, Dharwad 580001, Karnataka, India

*E-Mail: blaise.lobo@gmail.com

Abstract: Polyvinyl alcohol (PVA) – Polyvinyl pyrrolidone (PVP) blend films doped with low and moderate levels (from 0.004 Wt. % up to 3.8 Wt. %) of potassium permanganate ($KMnO_4$) were prepared by solution casting technique. The prepared films were characterized using optical/UV-Vis-NIR spectroscopy to yield optical band gap information and values of various optical parameters. The optical spectra of PVA-PVP blend films show significant changes, with increase in concentration of the strong oxidizing agent, $KMnO_4$. The UV-Visible spectra shows formation of intermediate absorption bands due to the formation of energy bands in the forbidden gap of PVA-PVP blend beyond 0.2 Wt.%. There is a prominent sharp absorption band at 3.5 eV for samples doped from 0.5 Wt. % up to 3.8 Wt. %. The optical constants like refractive index, extinction coefficient, and optical dielectric constants of these films were extracted from transmittance and reflectance spectra. The optical parameters, including the band-gap of PVA-PVP blend films can be controlled by optimizing the doping level.

Keywords: UV-Visible Spectra, potassium permanganate, PVA- PVP, blend, Optical parameters.

INTRODUCTION:

In recent years, the field of polymer science has seen preparation of a variety of polymeric blends to suit various applications, rather than the discovery of a new polymer itself. Polymer blending technology has been a versatile and economical strategy for designing new materials, with unique properties which can fulfill the demands of performance. Polymer blends have superior properties, when compared to the constituent homo-polymers. The blends of two or more polymers may or may not be chemically miscible [1, 2]. The structural, optical and electrical properties of polymeric materials can be enhanced and optimized by addition of a suitable dopant [3-6].

Optical characterization of materials provides vital information regarding the optical band gap and energy band structure of the material. It helps to elucidate various optical parameters. The study of optical properties (and optical parameters) has become important as it is necessary to predict use of the polymeric blend in optoelectronic and interference devices. For example, the study of refractive index of a material plays an important role in designing of optical fibers, prisms and optical windows [7, 8]. The study of absorption spectra, especially the absorption edge, gives information

regarding the electronic structure and the type of optical transitions.

Polyvinyl alcohol (PVA) is water soluble synthetic polymer. The unique properties of PVA are due to its semi-crystalline nature. PVA is preferred as one of the components in the preparation of a hydrophilic blend, due to its biodegradability, thermal stability, good solubility, mechanical flexibility, resistance to organic solvents and also because of it finds application as a biomedical material [9, 10]. Polyvinyl pyrrolidone (PVP) is a polymeric material, which is amorphous in nature. The advantages of PVP include non-toxicity, moderate electrical conductivity, environmental stability and ease of processing.

PVA and PVP are water soluble, miscible polymeric materials. PVA-PVP blend in the ratio 1:1 is found to be suitable for investigation of optical properties [11]. The interactions between the functional groups play a major role in miscibility of blends. Likewise, in case of PVA-PVP blend, the electrostatic interaction between the polar carbonyl group of PVP and hydroxyl group of PVA is responsible for their miscibility [12, 13]. PVA-PVP blend provides good charge storage capacity and is amenable to dopant addition [14]. The structural, optical and thermal properties of a polymer matrix can be tailored by addition of a suitable dopant [15]. Potassium permanganate ($KMnO_4$) is a strong oxidizing agent and an environmental friendly, water soluble material. It is used as water disinfectant in the treatment of waste water, to kill algae and to oxidize toxic materials [16].

In this paper, we present the preparation and characterization of $KMnO_4$ doped PVA-PVP blend films. Literature survey reveals that PVA-PVP blend doped with $KMnO_4$ has not been studied earlier, but $KMnO_4$ doped (oxidized) PVA films have been studied [17]. These studies revealed a decrease in the optical band gap with increase in dopant concentration. There is also an increase in the degree of crystallinity of KMnO4 oxidized PVA films with an initial increase in dopant concentration (that is, at low dopant concentration), followed by a decrease in crystallinity, at higher concentrations of the oxidizer.

EXPERIMENTAL:

Sample preparation:

$KMnO_4$ doped PVA-PVP blend films were prepared by solution cast technique. A standard solution of $KMnO_4$ was prepared in doubly distilled water. Equal weights of PVA and PVP (1:1) were dissolved in doubly distilled water, with constant stirring, until complete dissolution was achieved at room temperature. Later, this blend solution was filtered. After filtration, the blend solutions were doped with different dopant concentrations of standard $KMnO_4$ solution, and stirred continuously at room temperature to ensure complete interaction (between PVA/PVP and $KMnO_4$). The doped solutions of aqueous PVA-PVP blend thus prepared were poured into clean petri-dishes, and dried in an air cooled, temperature controlled oven maintained at 42°C. After drying, the films were carefully peeled from the substrate, properly labeled and stored in a desiccator, for further study. Films with doping level (expressed in Weight % (Wt. %)) from 0.004 to 3.8 Wt. % were prepared.

UV-Visible spectra:

Optical absorption spectra for oxidized PVA-PVP films were obtained by using Hitachi U 3310 UV-Visible spectrometer in the wavelength range 200-1000 nm at room temperature. The obtained spectra were analyzed to extract band gap information and determine various parameters.

RESULTS AND DISCUSSION:

Optical analysis:

Absorption co-efficient (α) as a function of wavelength was determined, according to equation (1).

$$\alpha = 2.303 \times \frac{A}{d} \quad \text{----- (1)}$$

In equation (1), A is the absorbance and d is thickness of the film.

Mott-Davis model can be used to determine the optical band gap, E_g, by applying equation (2) [18, 19] .

$$\alpha(\nu)\, h\nu = B\,(h\nu - E_g)^m \quad \text{-----(2)}$$

In equation (2), B is the disorder parameter and E_g is the optical energy band gap of the polymeric material. The possible values of m are ½, 3/2, 2 and 1/3, corresponding to direct allowed transition, direct forbidden transition, indirect allowed transition and indirect forbidden transition, respectively. The nature of optical transition was found to be indirect allowed transition (best fit). The fit for direct allowed transitions was also found to be satisfactory.

The energy, E, of incident photon was calculated using equation (3).

$$E = (1.24 \times 10^{-6})/\lambda \quad \text{----- (3)}$$

In equation (3), the wavelength of incident photon, λ, is expressed in meter (m) and the incident photon energy, E, is expressed in electron volt (eV).

Activation energy, E_a, corresponding to the optical absorption edge was determined by extrapolating linear region of the α versus E graph to zero absorption value. Figure 1 shows a plot of absorption coefficient (α) versus photon energy ($h\nu$) for low doping levels, and the figure inset therein shows α versus $h\nu$ plot for higher doping levels; that is, from 0.4 Wt.% up to 3.8 Wt. % of $KMnO_4$ in PVA-PVP blend.

Figure 2 shows the determination of band gaps corresponding to indirect allowed transitions, using the $(\alpha h\nu)^{1/2}$ versus $h\nu$ graph, for films doped from 0.5 Wt. % up to 3.8 Wt.%. A red shift in the absorption edge of the optical spectra was observed for low dopant concentrations, from 0.04 Wt.% up to 0.30 Wt.%, but at 0.40 Wt.% and above, a blue shift was observed. At the same time, a sharp intermediate absorption band was observed at 0.19 eV for 0.5 Wt. % doping level. The optical spectrum of film with doping level (DL) 1.0 Wt. % showed two intermediate bands; at 2.71 eV and 3.34 eV, respectively. Figure 1.a and 1.b illustrate the simplified band structure, for doping levels 0.5 Wt. % and 1 Wt. %, respectively.

The width of intermediate energy bands for 0.5 Wt.% was 0.2eV and for 1Wt.% DL, the width of intermediate bands were 0.36 eV and 0.67eV. The presence of intermediate absorption bands in this wavelength region suggests the potential for application of this material in solar devices. The changes in the band structure of PVA-PVP blend with the increase in $KMnO_4$ content may be attributed to ionic complex formation. Disorder or

imperfections introduced in PVA-PVP matrix by potassium (K+) ions produces localized states of various depths in the forbidden gap of PVA-PVP blend, which is evidenced by formation of the intermediate absorption band.

Table 1: *Values of activation energy and indirect band gap in the case of $KMnO_4$ doped PVA-PVP blend films. Here, α_1 and α_2 are symbols for activation energy. E_{i1} and E_{i2} refer to the band gap for indirect allowed transitions.*

DL (Wt.%)	α_1 (eV)	α_2 (eV)	E_{i1} (eV)	E_{i2} (eV)
0.00	5.04	-	4.80	-
0.004	4.70	-	4.20	-
0.03	4.94	-	4.65	-
0.10	5.01	-	4.94	-
0.20	5.02	-	4.83	-
0.30	5.02	-	4.76	-
0.40	5.42	-	5.20	-
0.50	5.34	3.49	5.17	3.41
1.00	5.36	3.36	5.19	3.31
3.80	-	3.50	-	3.37

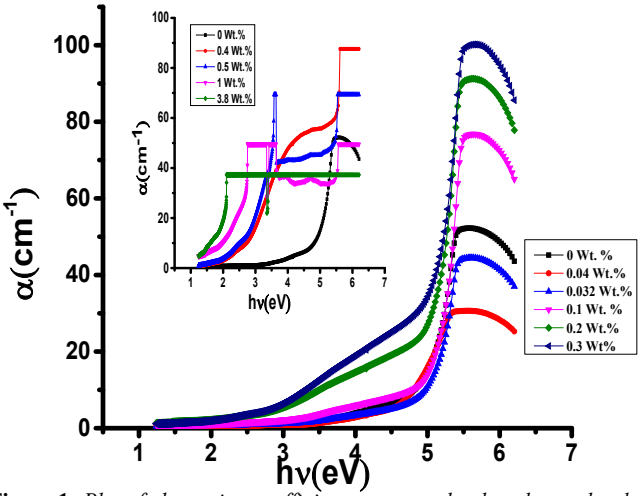

Figure 1: *Plot of absorption coefficient α versus hν low dopant levels. Inset show plot of absorption coefficient α versus hν for high dopant levels.*

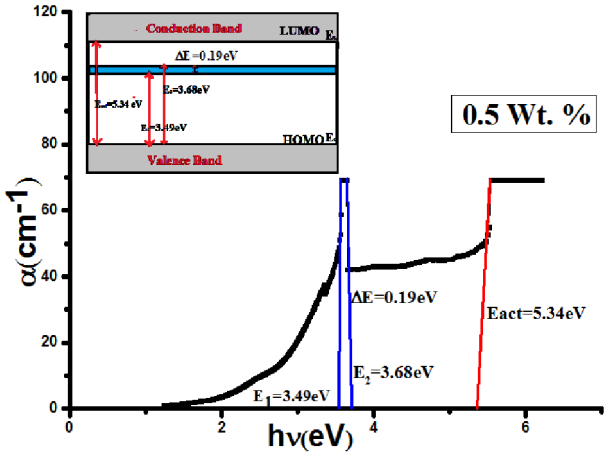

Figure 1.a: *Illustration of band structure for 0.5 Wt.%*

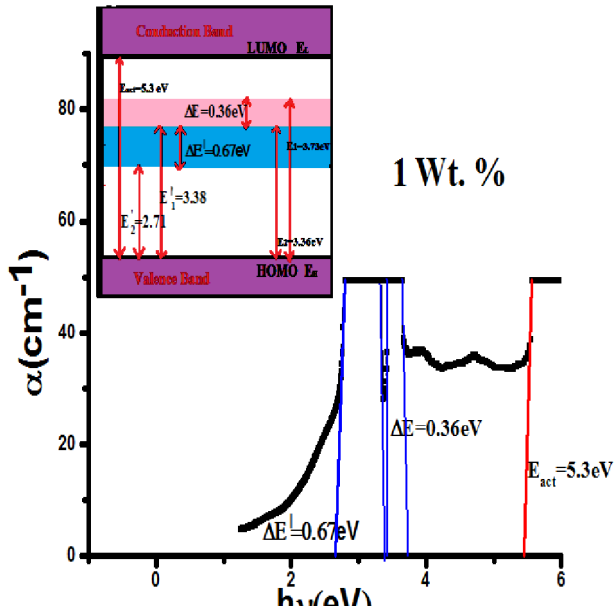

Figure 2.b: *Illustration of band structure for 1 Wt.%*

Optical constants:

Optical constants like Refractive index n and the extinction coefficient k, were calculated from fundamental relations of photon transmittance (T) and absorbance (A).

Reflectance (R) is determined by equation (4).

A+T+R=1 ------- (4)

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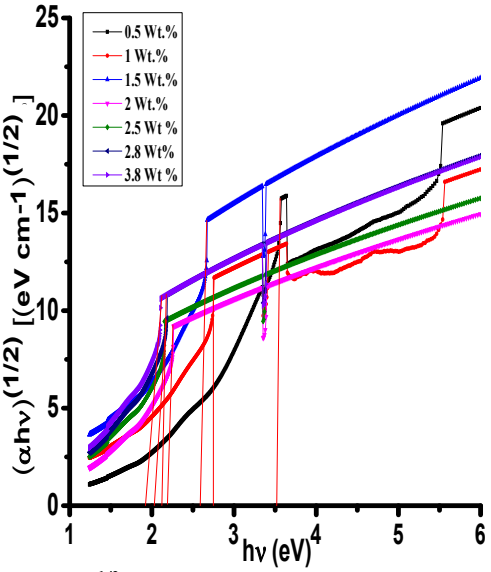

Figure 2: *Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ 0.5 Wt.% to 3.8 Wt.% showing intermediate absorption bands.*

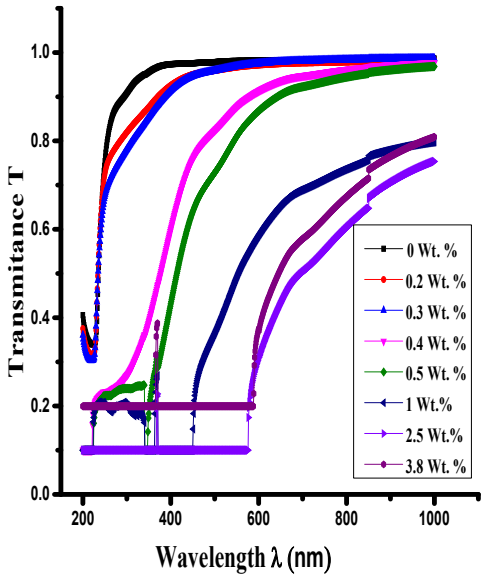

Figure3.a: *Transmittance spectra for low and high dopant levels.*

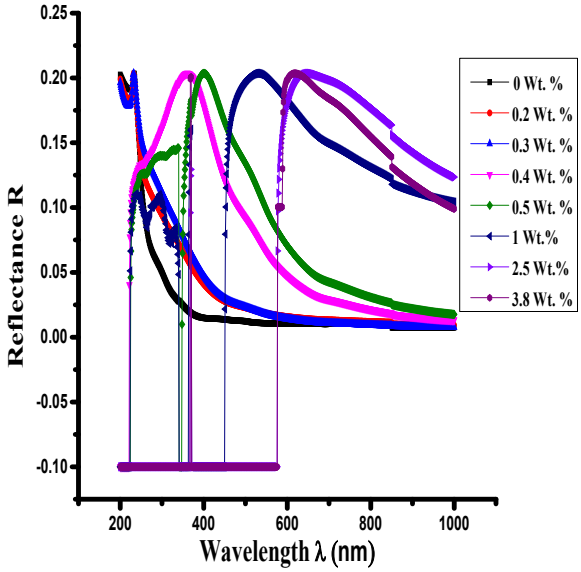

Figure 3.b: *Reflectance spectra for low and high dopant levels.*

In equation (4), A is Absorbance, T is Transmittance and R is Reflectance of the sample. The figure 3.a and figure 3.b show the transmittance and reflectance spectra, respectively.

Thus, an increase in the transmittance (T) with increase in wavelength, and decrease in T with

increase in dopant concentration is observed. This may be due to following reasons: T depends on surface roughness, as surface scattering reduces with a decrease in roughness. Higher value of transmittance with decrease in dopant concentration is due to impurity centers induced by dopant. The reflectance spectra show two regions; first, there is an increase in reflectance with wavelength, and later, it is reduced. The study of refractive index of a material is necessary to understand the electronic polarization of ions, field in the material and predict their use as an efficient optical material.

Refactive index is given by Fresnel formula

$$n = \left(\frac{1+R}{1-R}\right) - \sqrt{\frac{4R}{(1-R)^2} - k^2} \qquad \text{----- (5)}$$

In equation (5), k is the extinction coefficient, given by equation (6).

$$k = \frac{\alpha\lambda}{4\pi} \qquad \text{----- (6)}$$

Figures 4.a and 4.b show the variation of n and k with respect to wavelength, λ, respectively .

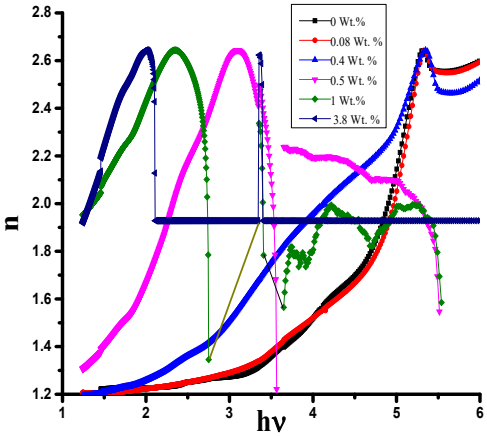

Figure 4.a: *Variation of refractive index n with wavelength λ.*

The refractive index is higher at lower λ; this is due to the interactions taking place between electrons and photons. The value of k increases with increase in dopant concentration, which is due to surface roughness or disorder, as is evident by increased scattering losses and thereby, reduced transmitting ability.

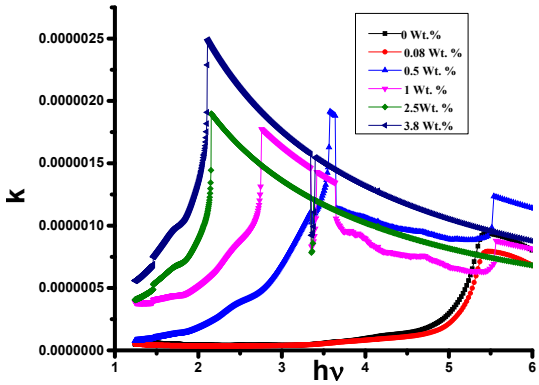

Figure 4.b: *Plot of Extinction coefficient k versus Wavelength λ*

The values of the real and imaginary part of dielectric contants with respect to energy and dopant level are shown in figures 5.a and 5.b , respectively. The Real part of dielectric constant is given by the relation shown in equation (7).

$$\epsilon_r = n^2 - k^2 \qquad \text{----- (7)}$$

The behavior of ϵ_r is similar to that of refractive index (n) because of the smaller values k^2, when compared with n^2 .

ϵ_i depends on k, which in turn related to absorption coefficient, α (see equation 8).

$$\epsilon_i = 2nk \qquad \text{----- (8)}$$

Both ϵ_r and ϵ_i increase with increase in dopant concentration.

CONCLUSIONS:

$KMnO_4$ doped PVA-PVP blend films were prepared in the doping range, varying from 0.012 wt% up to 3.8 wt%, and their optical properties were investigated. The analysis of optical (UV-Vis) spectra reveals formation of

intermediate energy bands within the forbidden gap of PVA-PVP, on doping with $KMnO_4$. Optical constants and parameters were determined.

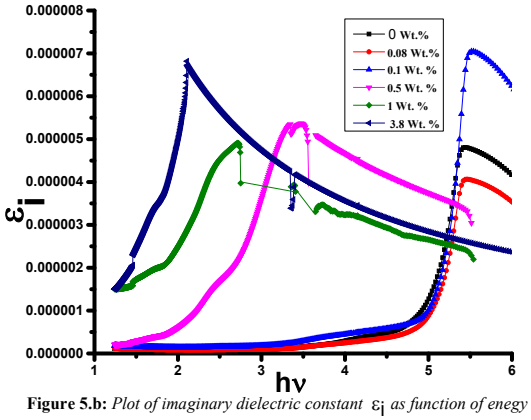

Figure 5.b: *Plot of imaginary dielectric constant* ε_i *as function of enegy h v.*

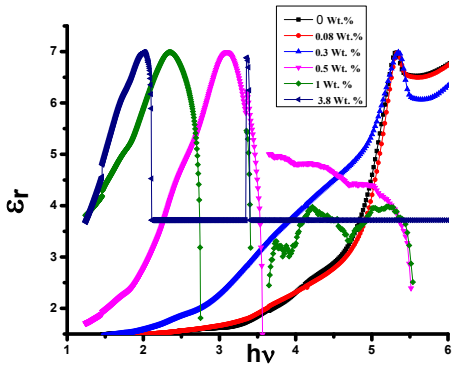

Figure 5.a: *Plot of real dielectric constant* ε_r *as function of enegy h v.*

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