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Dispersion Parameters of Polyvinyl Alcohol Films doped with Fe

Nadir F Habubi¹, Khalid H Abass², Chiad S Sami¹, Duha M A Latif³, Jandow N Nidhal¹, A Ismaeel Al Baidhany¹

¹Department of Physics, College of Education, Mustansiriyah University, Baghdad, Iraq

²Department of Physics, College of Education for Pure Sciences, University of Babylon, Babylon, Iraq

³Department of Physics, College of Education for Pure Sciences, University of Baghdad, Baghdad, Iraq.

nadirfadhil@uomustansiriyah.edu.iq, pure.khalid.haneen@uobabylon.edu.iq,
dr.sami@uomustansiriyah.edu.iq, nidhaljandow@uomustansiriyah.edu.iq,
ismaeel_2000@uomustansiriyah.edu.iq.

Abstract. Polyvinyl alcohol polymer was dissolved in water in order to prepare films with different concentration of Fe utilizing casting method. The optical properties were obtained by recording the transmittance spectrum in the wavelength range (300-900) nm. The dispersion parameters were calculated using the Wemple–DiDomenico method. Dispersion energy (E_d) and the single oscillator energy of electronic transition (E_o) were decreased with the increasing of Fe content in the PVA-Fe films. While Urbach energy was increased. The energy gap decreased from 4.08 eV to 3.52 eV for PVA: 4% Fe film.

1. Introduction

PVA has attained great importance due to, its high dielectric strength, high charge storage capacity. Electrical and optical properties of PVA can be tailored by doping. It was notified that the PVA based electrolyte contains water, which improves the conductivity and maintains the dimensional constancy of the electrolyte [1]. Polymers doped with metal particles helps in enhancing the kinetics of the ionic species through the compound by motivating better vicinity of the required ions within the polymer/metal composite [2], and its (Metal/polymer composites) have appealing great importance in recent years because of the unique properties of metals and polymers built into them. The doping transition metal halides into PVA are serious for limiting and monitoring the operational characteristic of the different PVA composites [3, 4].

Polymer blends were taken place in the vision of broad application concerning systems and devices. The addition of dopant to the polymer matrix will affect electrical, electrochemical and optical properties and can be tuned to obtain new properties for diverse applications [5, 6]. In this study, the prepare of PVA-Fe composite was done by casting solution method and the study of Urbach energy and dispersion parameters of this composite were obtained.



2. Materials and Methods

Matrix Polymer of polyvinyl alcohol with molecular weight 10000 g/mol (supplied from BDH Chemicals England) was employed to obtain a polymeric Solution. FeCl_3 (supplied from Metck Chemicals Germany) was used as a doping agent embedded in PVA matrix with (2% and 4%) volumetric concentration. This composite was deposited by casting method at ambient temperature to obtain films in order to study their optical properties. Transmittance and absorbance spectra were recorded by spectrophotometer Shimadzu (Japan) in the wavelength range (300-900 nm).

3. Results and discussion

Transmittance spectra of PVA-Fe with various content of Fe are registered by spectrophotometer in the range 300-900 nm. Transmittance against wavelength is presented in 'figure 1', which shows that the transmittance decreased with the increasing of Fe content in the PVA-Fe films, make these films less transparency.

'Figure 2' shows the variation of reflectance with a wavelength of PVA-Fe films. The reflectance increased sharply with the increase of wavelength until 500 nm and decreased with the increasing of Fe content in this region, while it's taken stable values with wavelength until 900 nm of wavelength and changed slightly with increasing Fe content.

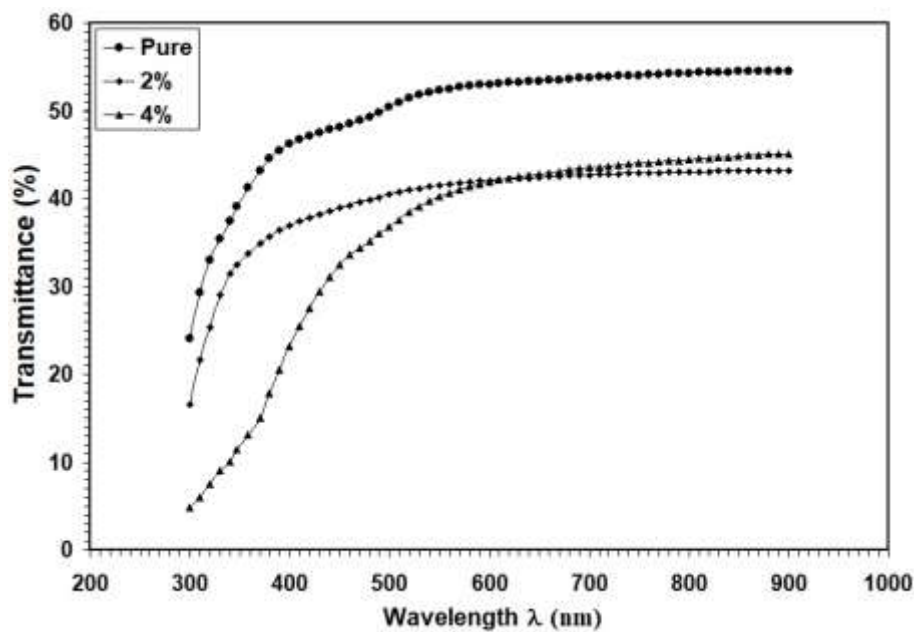


Figure 1. Transmittance via wavelength of PVA-Fe composite with various content of Fe.

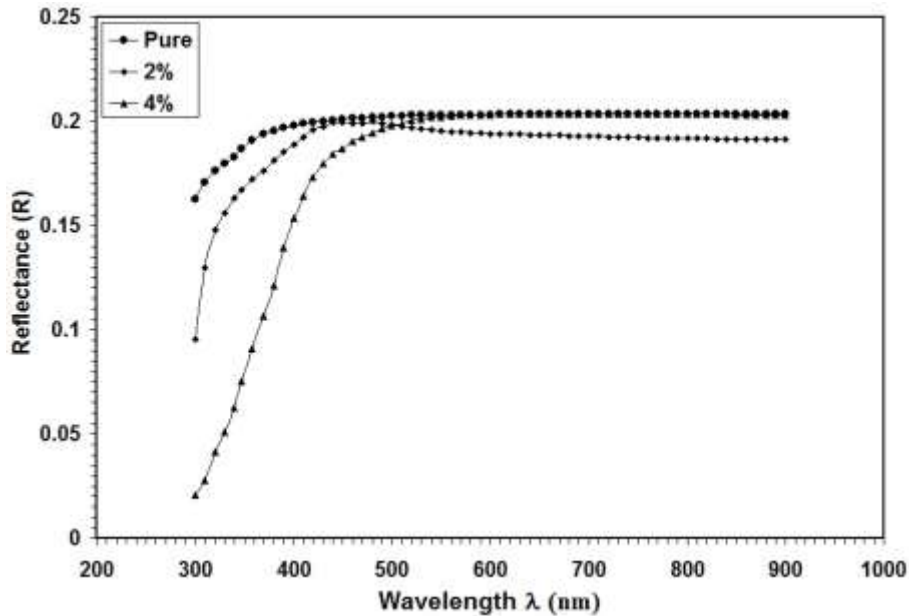


Figure 2. The refractive spectra of PVA-Fe composite with various content of Fe.

Real (ϵ_r) and imaginary (ϵ_i) parts of dielectric constant are calculated ‘as in equation (1) and equation (2)’ [7]:

$$\epsilon_1 = n^2 - k^2 \quad (1)$$

$$\epsilon_2 = 2nk \quad (2)$$

Where (n) is the index of refraction and (k) is the extinction coefficient. The variations of these parameters PVA-Fe wavelength are presented in ‘figures 3’ and ‘figures 4’. From these figures, it can be seen that both parts are decreased with the increasing of Fe content.

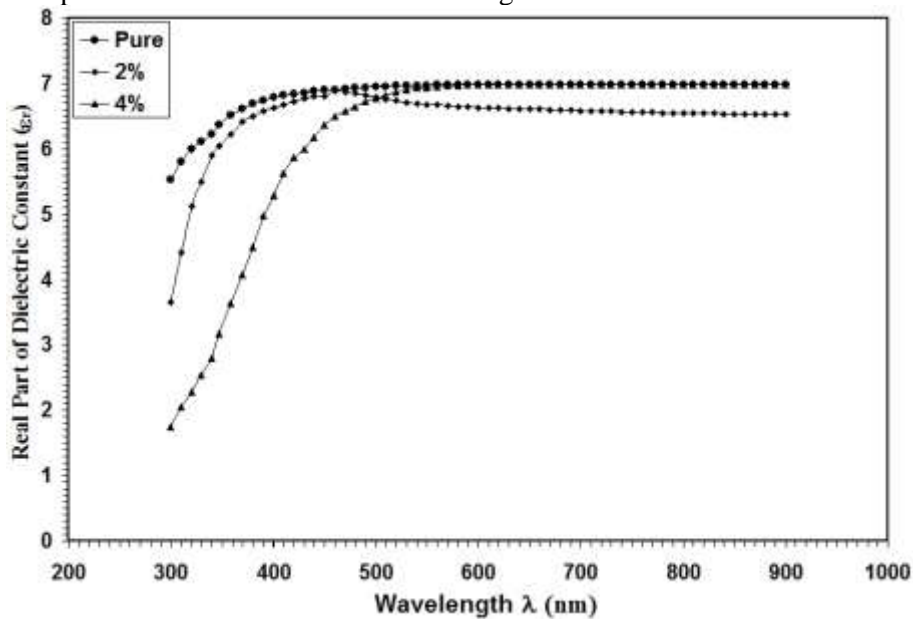


Figure 3. The real part of the dielectric constant of PVA-Fe composite with various content of Fe.

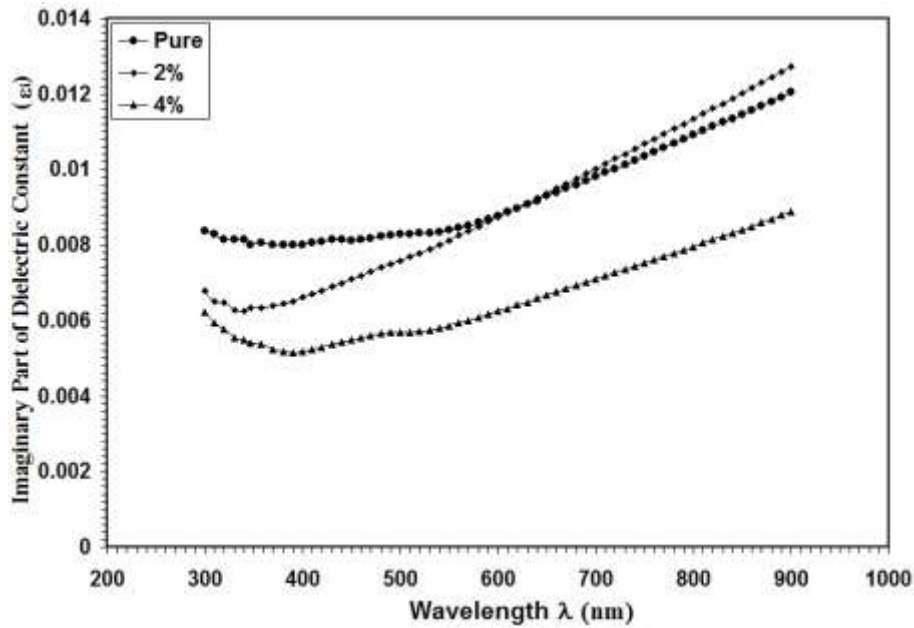


Figure 4. The imaginary part of the dielectric constant of PVA-Fe composite with various content of Fe.

The Urbach energy (E_U) was mentioned to the width of the exponential absorption edge, also called Urbach tails [8]. It can determine 'as in equation (3)' [9]:

$$\alpha = \alpha_0 \exp\left(\frac{E}{E_U}\right) \quad (3)$$

Where (E) denoted photon energy and (α_0) is fixed. Variations of $\ln \alpha$ with photon energy ($h\nu$) for PVA-Fe films are presented in 'figure 5'. The values of Urbach energy for PVA-Fe films are listed in (table 1), which increased with the increasing of Fe content in the PVA-Fe films.

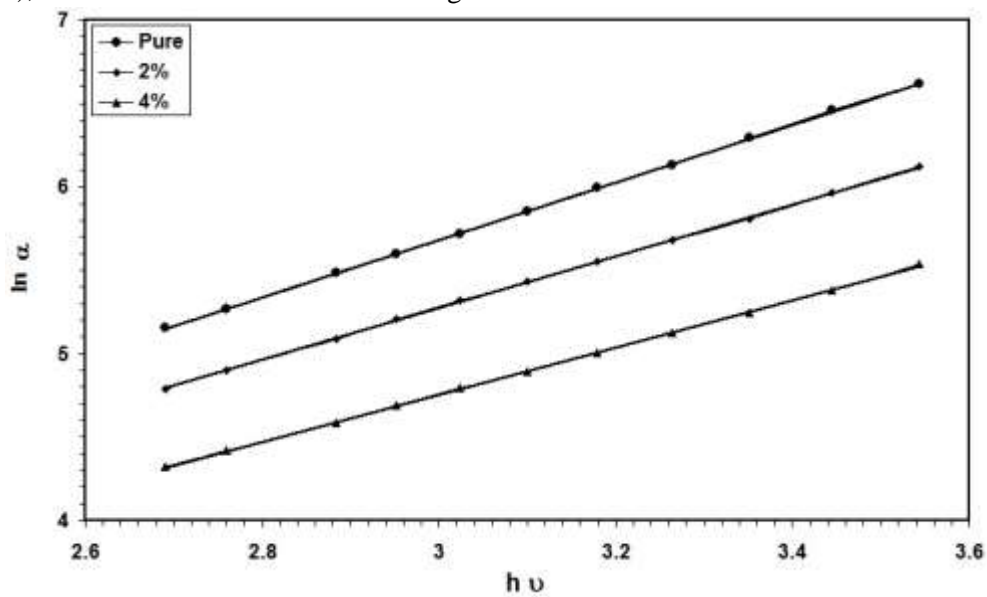


Figure 5. The Urbach energy of PVA-Fe composite with various content of Fe.

The dispersion parameters are very important in many applications such as optical communication and in the design of optical devices [10]. From Wemple–DiDomenico it can describe the dispersion parameters ‘as in equation (4)’ [11]:

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

Where E_d is the dispersion energy, E_o denotes single oscillator energy of the electronic transition, and n denotes refractive index. To estimate the values of E_d and E_o , it can plot $(n^2-1)^{-1}$ in the x-axis and $(h\nu)^2$ in the y-axis, as shown in Figure 6. E_d and E_o were obtained from slope $(E_d E_o)^{-1}$ and opposed (E_o/E_d) [12]. Energy gap (E_g) values were estimated from the energy of the single oscillator of the relation $E_o \approx E_g$ [12]. The values of E_d , E_o , and E_g are listed in (table 1). From the Table, the values of E_d , E_o , and E_g decrease with the increasing of Fe content in the PVA-Fe films. The index of refraction (n_∞) for the PVA-Fe films were gained by the interception of the perpendicular axis in Figure 6.

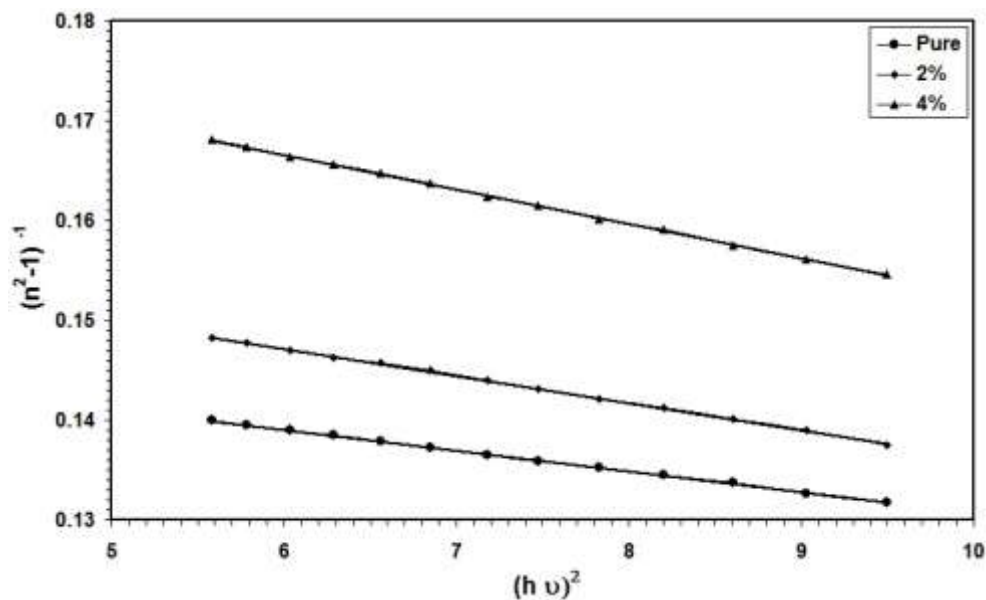


Figure 6. The $(n^2-1)^{-1}$ versus $(h\nu)^2$ of PVA-Fe composite with various content of Fe.

The Sellmier or Cauchy expressions for the refractive index depends on the wavelength ($n(\lambda)$) which are purely mathematical fitting ‘as in equation (5)’ [11]:

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

Where λ_o denote the average oscillator position and S_o denote the average oscillator strength. These parameters can be determined from the plot of $(n^2-1)^{-1}$ versus λ^2 as illustrated in ‘figure 7’. The slope who produces straight line accord $1/S_o$, and the infinite-wavelength intercept accord $1/S_o \lambda_o^2$ [13]. The values of S_o and λ_o are recorded in (table 1). The value of S_o was increased with the increase of Fe content in the PVA-Fe films, while λ_o value was decreased.

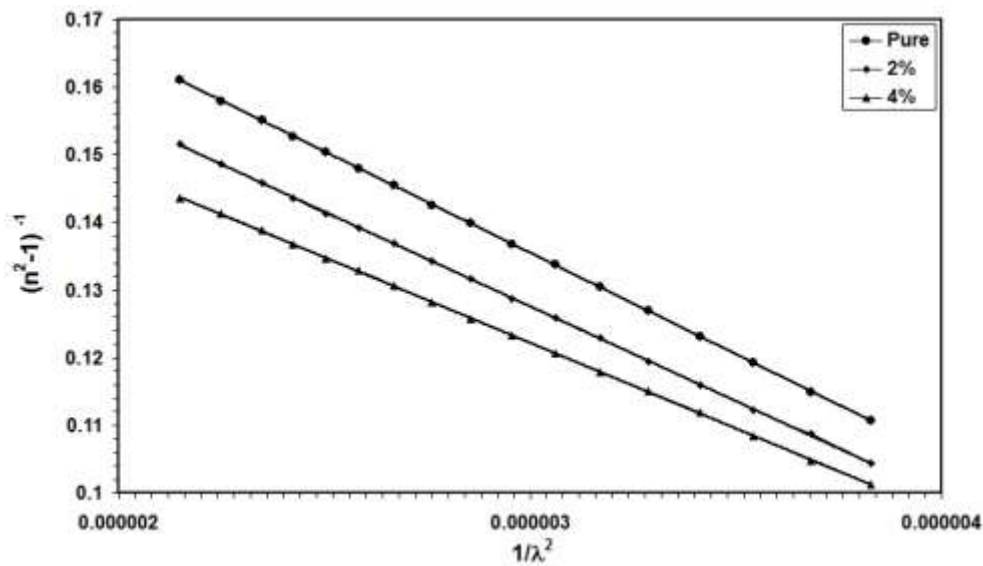


Figure 7. The $(n^2-1)^{-1}$ versus $1/\lambda^2$ of PVA-Fe composite with various content of Fe.

The moments of the imaginary part of the optical spectrum (M_{-1} , M_{-3}) of PVA-Fe films are estimated 'as in equation (6) and equation (7)' [14]:

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

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

Values of M_{-1} and M_{-3} are recorded by Table (1). From the Table, It could be noticed that optical moments M_{-1} , M_{-3} decrease by the increasing of Fe content in the PVA-Fe films.

Table. Optical parameters of PVA-Fe composite with various content of Fe.

PVA and doped PVA	E_d (eV)	E_o (eV)	E_g (eV)	ϵ_∞	$n(o)$	M_{-1}	M_{-3} eV ⁻²	$S_o \times 10^{13}$ m ⁻²	λ_o nm	E_U meV
Pure	58.32	8.16	4.08	8.14	2.85	7.14	0.127	3.33	426	588
2 %	49.69	7.45	3.72	7.66	2.77	6.67	0.120	3.57	410	649
4 %	41.47	7.05	3.52	6.88	2.62	5.88	0.118	4.00	387	709

4. Conclusion

Polyvinyl alcohol polymer was dissolved by water to prepare films with various content of Fe by solution casting method. The Urbach energy was increased with the increase of Fe content in the PVA-Fe films, while the energy gap decreased that calculate using Wemple–DiDomenico equation. Dispersion energy (E_d) and single oscillator energy of electronic transition (E_o) decrease with increasing of Fe content in the PVA-Fe films.

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