Enhancement of Urbach Energy and Dispersion Parameters of Polyvinyl Alcohol with Kaolin Additive

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Abstract

Polyvinyl alcohol films have been prepared with various additives of Kaolin by casting method at a thickness of 10 µm. The impacts of Kaolin additive on some optical parameters has been studied by recording the transmittance spectra UV-Visible spectrophotometer in the range 200-900 nm after studied the structure from X-ray diffraction and FTIR to determine the crystallites and the activation groups. Urbach energy increased with the increases of Kaolin additive leading to decrease bandgap from 4.08 eV of PVA film to 3.77 eV of 4% Kaolin additives.

Key Words: Polyvinyl Alcohol, Kaolin, XRD, Dispersion Parameters, Urbach Energy.

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Introduction

There are huge works on PVA with various additives to get better characteristics [1, 2]. PVA is highly biocompatible, biodegradable and nontoxic material, and has convenient chemical and thermal stability [3]. Hence wide applications in optical and electronic devices concerning PVA [4]. Clays are organically modified and ha many applications especially in the with polymers as additives [5]. Recent work concerning the PVA matrix such as Mallakpour and Dinari fabricate poly (vinyl alcohol) (PVA)/nano-clay nanocomposite films [6]. The same authors succeed to prepare PVA and adjust chiral layered double hydroxides [7]. Casting method is useful and important method to fabricate the polymer films [8-12]. This work aims to obtain the optical dispersion relation for pure PVA and PVA reinforced by Kaolin. Urbach energy was determined in this study.

Experimental Part

PVA with Mw 90000-100000 Supplied by (BDH Chemicals) was used as a host polymeric material in this work. Kaolin clay is available in the local area Dwekla with volumetric percentage of (2% and 4%). Films were deposited by casting technique at room temperature. Film thickness was measured by digital micrometer their values were around 10 µm. The structural properties were evaluated by XRD (Shimadzu, model: XRD-6000, Japan) with CuKα radiation (λCu=0.154056nm). The FT-IR spectrophotometer (Shimadzu, 4800S) within a range of 4000–400 cm−1 and KBr disc was used.

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Transmittance and absorbance spectra were registered via double beam spectrophotometer (Shimadzu UV Probe, Japan) to calculate some optical properties and dispersion parameters.

Results and Discussion

Fig.1 displays XRD patterns of PVA polymer and 2%, 4% concentration of Kaolin Dwekla. The result indicates that all the prepared films were amorphous as shown in the figure.

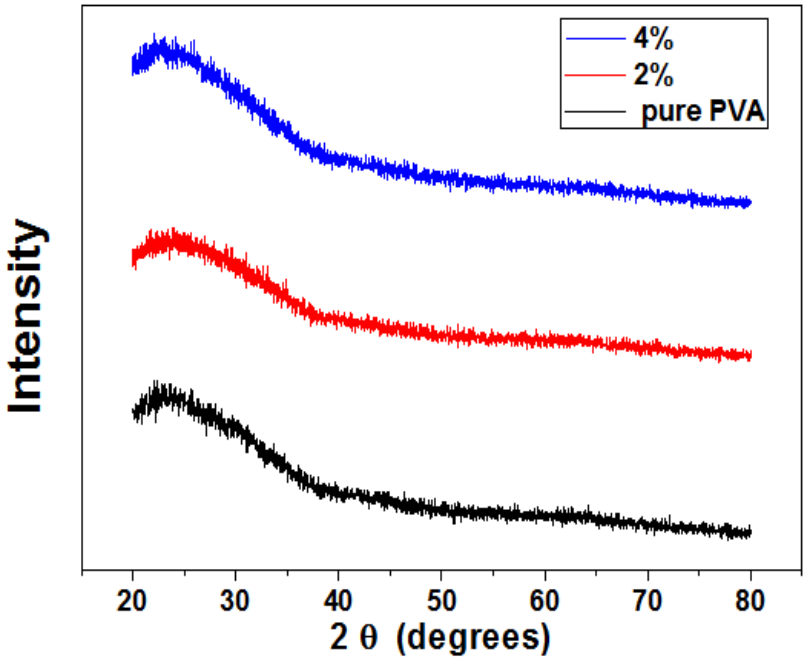
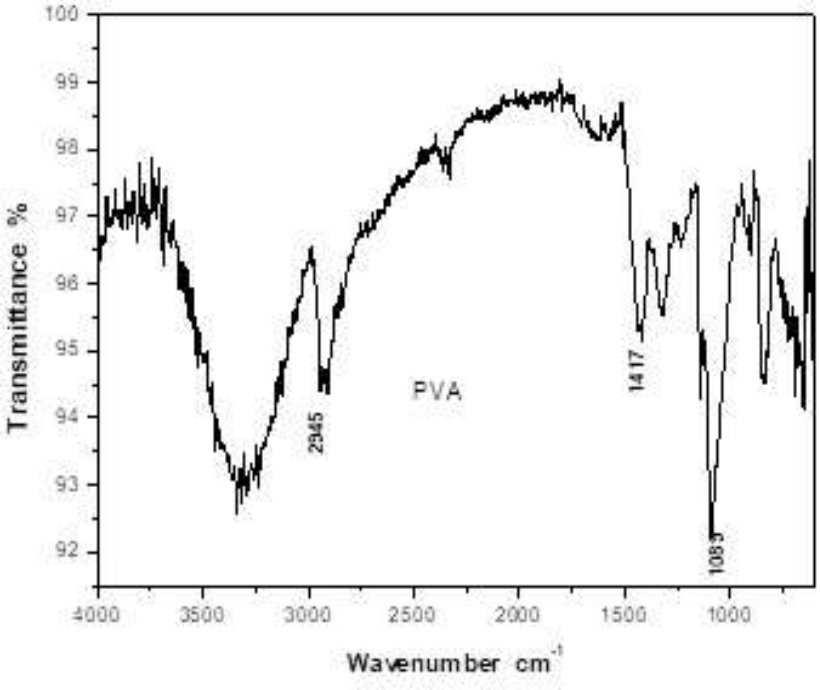


Fig. 1. XRD patterns of the deposited films.

The infrared spectra of PVA, PVA additive by 2% Kaolin and PVA doped by 4% Kaoline are shown in fig. 2. The absorption peaks in the zone of (2945, 2944) cm^{-1} are due to stretching vibrations of –CH and CH_2 groups. at (1417,1420) cm^{-1} associated with vibration of CH_2 bond in PVA molecules at about 1089 cm^{-1} for the –C–O group. OH stretching at (3694,3618) cm^{-1} band ,Bands corresponding to SiO stretching was 749 cm^{-1}, while SiO deformation bands were 1008 cm^{-1}, These results are nigh to the results gained for theoretical Kaolin. These results is very close to the results obtained by Ekosse [13] and Mallakpour and Dinari [14].



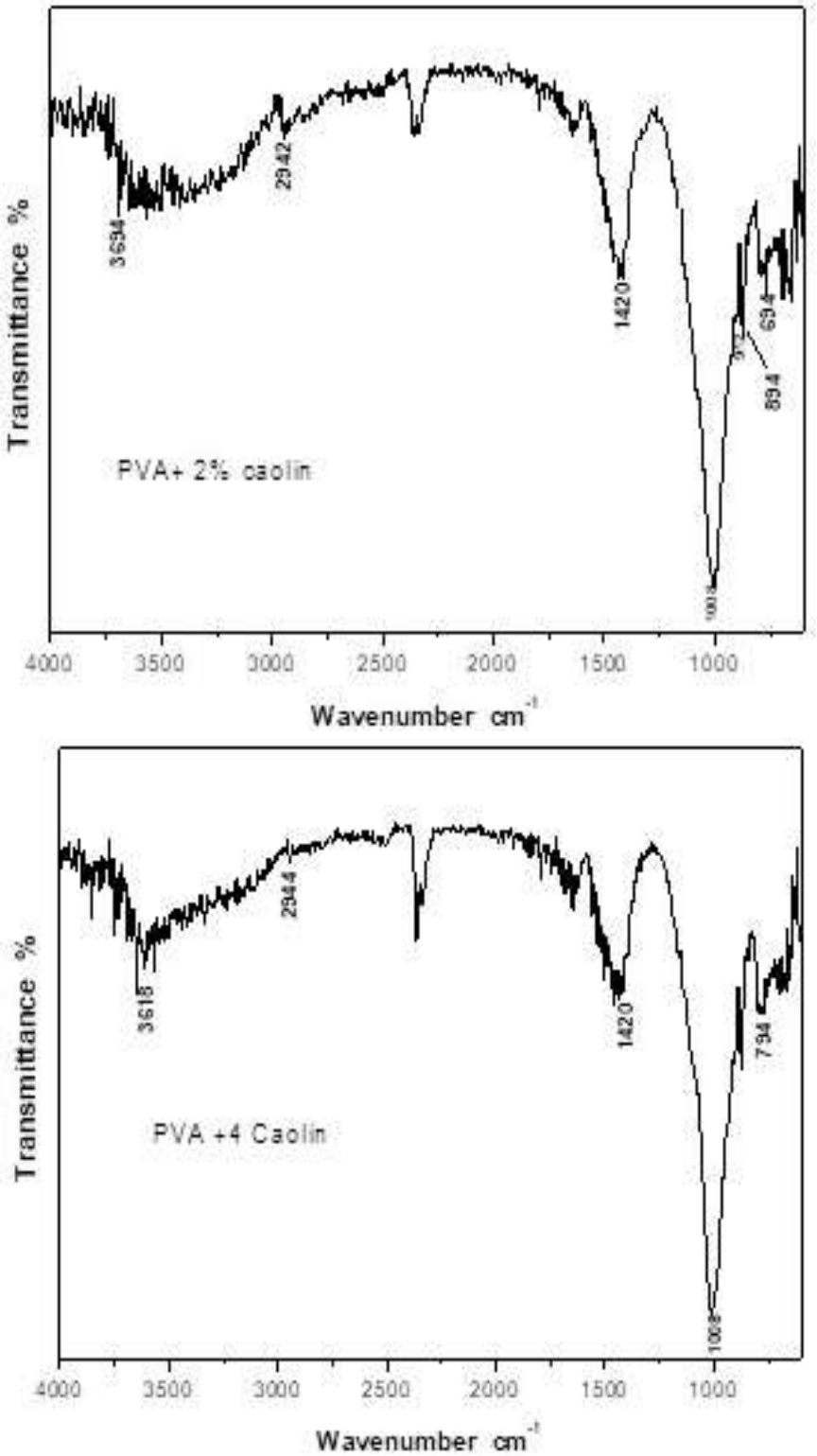


Fig. 2. FTIR spectra for the deposited films.

Transmittance spectra of the PVA-Kaolin films prepared by casting solution method is displayed in Fig. 3. The transmittance increased with increase of wavelength and decrease with the increase of Kaolin additive.

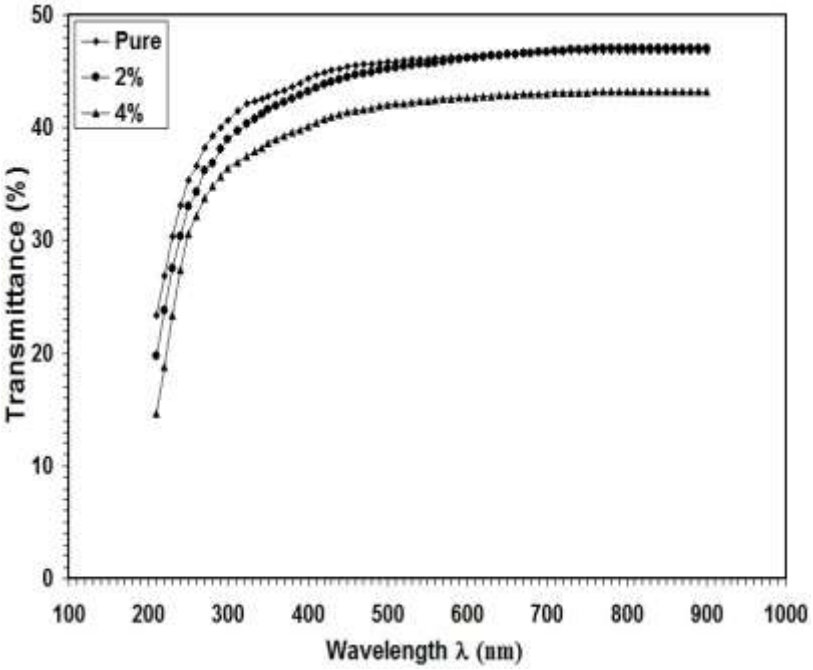


Fig. 3. Transmittance spectra versus wavelength of as prepared and Kaolin additive PVA films.

Fig.4 shows the reflectance spectra versus wavelength of PVA-Kaolin films. From the figure, the reflectance decrease with the increase Kaolin additive until 350 nm of wavelength, and then the reflectance unchanged.

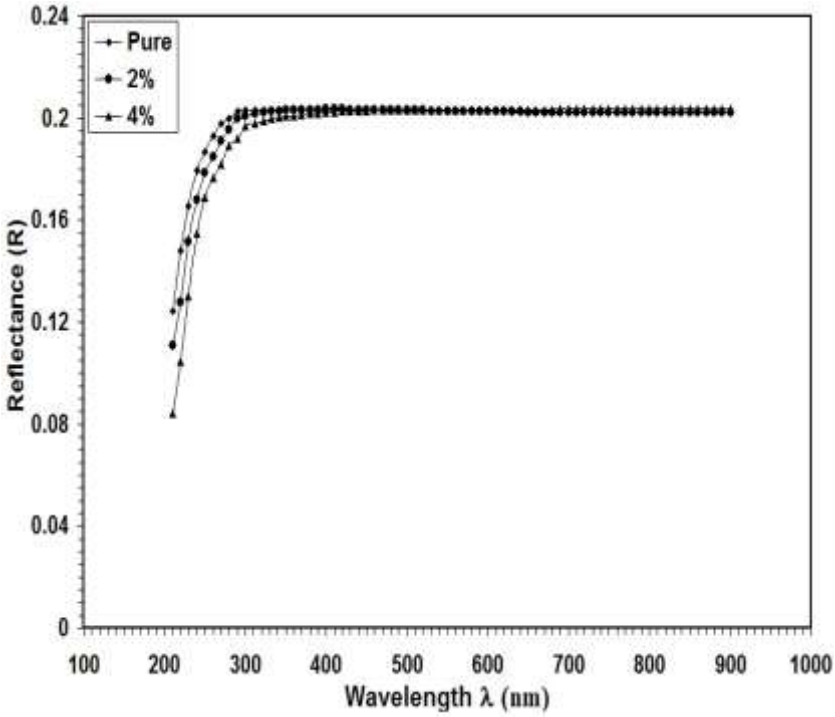


Fig. 4. Reflectance spectra versus wavelength of as prepared and Kaolin additive PVA films.

The real ε_r and imaginary ε_I dielectric constants are calculated by these relations [15]:

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

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

The rapport between ε_r, ε_I and the wavelength are shown in Figs.5 and 6. From these figures, we observe the decreases of ε_r with the increasing of Kaolin additive films until 350 nm of wavelength, and then ε_r unchanged with the increase of Kaolin additive in the region more than 350 nm. While ε_I increase with the increase of Kaolin additive as shown in Fig.6.

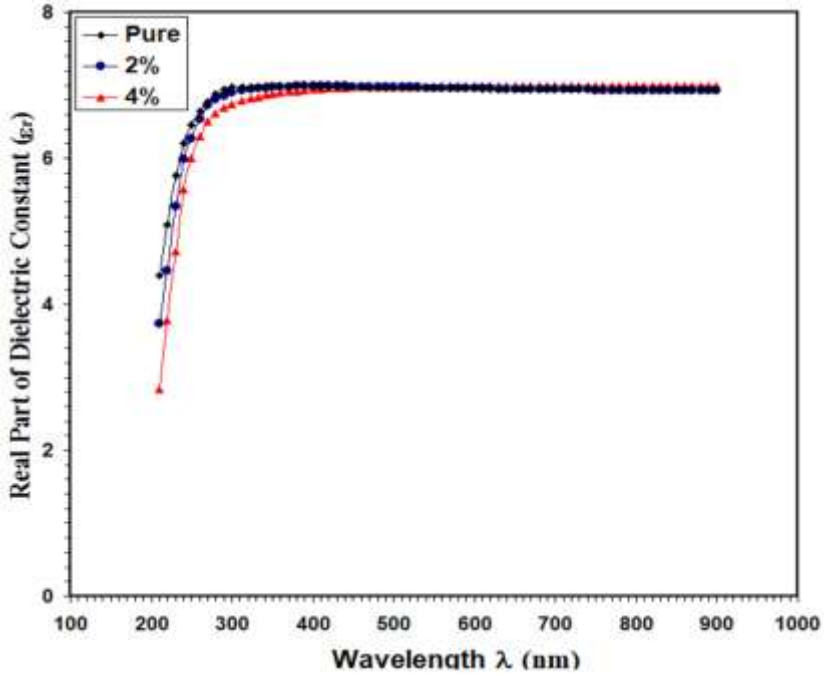


Fig. 5. ε_r versus wavelength of as prepared and Kaolin additive PVA films.

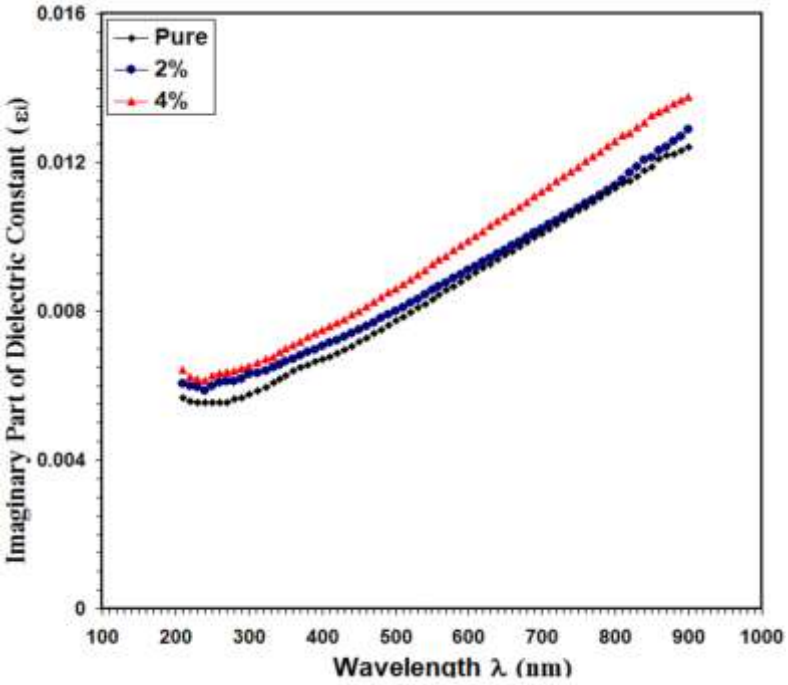


Fig.6. ε_i versus wavelength of as prepared and Kaolin additive PVA films.

The Urbach tails (E_U) represent the width of localized states inside the optical bandgap and was estimated from the following relation [16]:

$$\alpha = \alpha_o \exp\left(\frac{h\upsilon}{E_U}\right) \qquad (3)$$

Where $h\upsilon$ is photon energy and α_o is a constant. Fig.7 represents relationship between the $\ln\alpha$ and ($h\upsilon$). The reciprocal of the slop for the linear plots in Fig.5 represent the values of Urbach energy. The values of Urbach energy are increase with increasing of Kaolin additive in PVA-Kaolin films, which listed in Table (1).

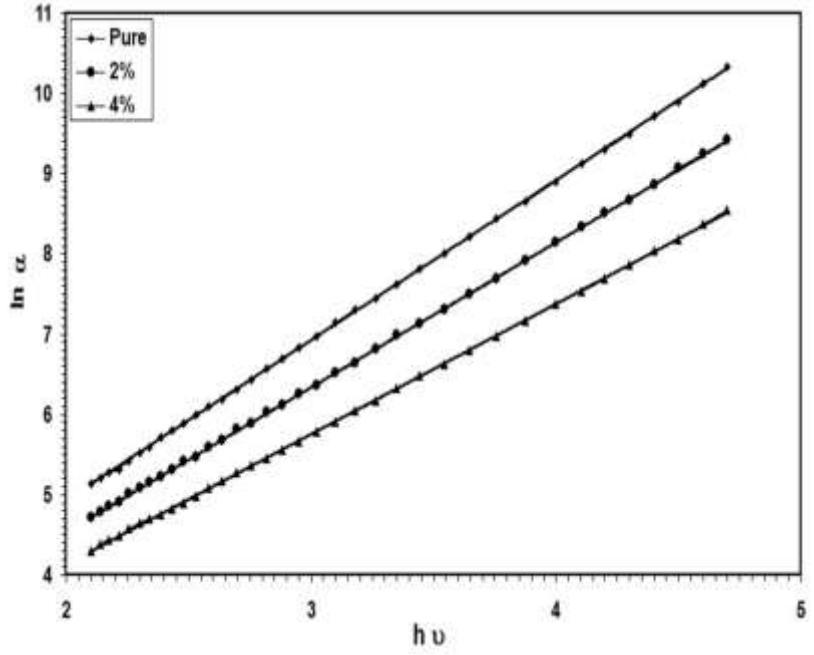


Fig. 7. lnα against photon energy (hυ) of as prepared and Kaolin additive PVA films.

The dispersion parameters introduced by Wemple, DiDomenico model for PVA-Kaolin films are determined via this relation [17]:

$$n^2 - 1 = [\, E_d E_o / E_o^2 - (h\upsilon)^2 \,] \qquad (4)$$

Where n is the refractive index, E_o is the oscillator energy and E_d is the dispersion energy related to the average strength of the optical transitions [18]. These parameters can be estimated from $(n^2\text{-}1)^{-1}$ on y-axis and $(h\upsilon)^2$ on x-axis, and it can use $(E_oE_d)^{-1}$ and intercept (E_o/E_d). Fig.8 represents the relationship between the $(n^2\text{-}1)^{-1}$ and $(h\upsilon)^2$.

The values of E_o and E_d decrease with the increase of Kaolin additive in the PVA-Kaolin films as displayed in Table (1). To determine the values bandgap (E_g), that can be obtained from the relation $E_o = 2E_g$ [19], these values are offered in Table 1.

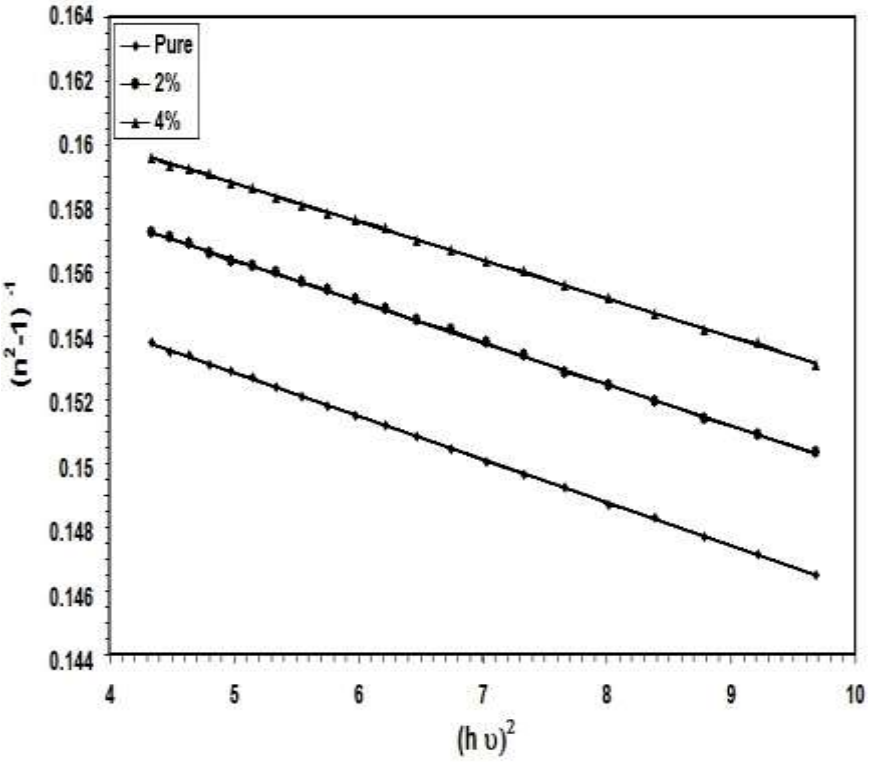


Fig. 8. $(n^2\text{-}1)^{-1}$ against $(h\upsilon)^2$ of as prepared and Kaolin additive PVA films

The average oscillator wavelength (λ_o), and oscillator length strength (S_o) of PVA-Kaolin films were estimated from single term Sellmaeir oscillator [20]:

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

To determine these values, Fig. 9 displays $(n^2\text{-}1)^{-1}$ that plotted against $1/\lambda^2$. The values are displayed in the same Table.

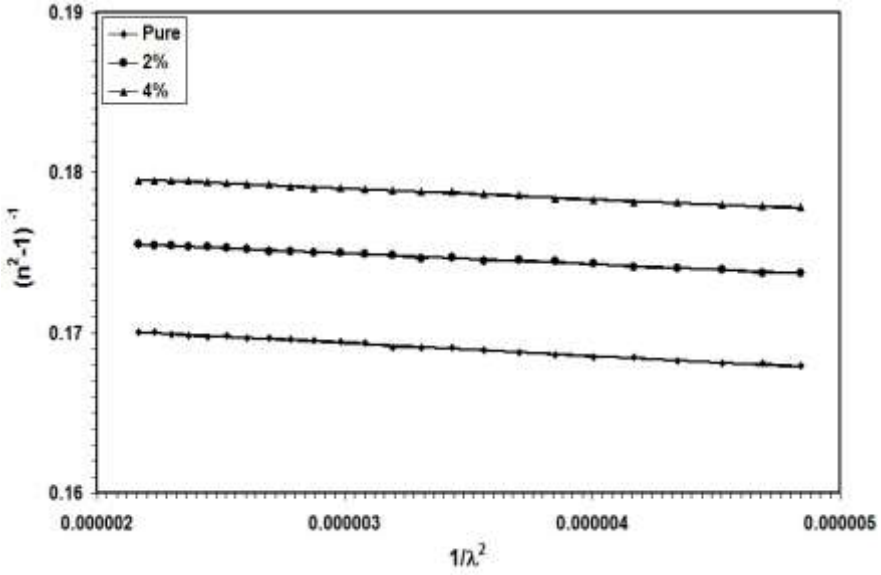


Fig. 9. $(n^2\text{-}1)^{-1}$ with $1/\lambda^2$ of as prepared and Kaolin additive PVA-Kaolin films.

The moments of the optical spectra (M_{-1}, M_{-3}) of PVA-Kaolin can determine from the equations [21]:

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

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

The values of optical spectra moments increase with the increase of Kaolin additive in the PVA-Kaolin films, as listed in Table (1). This Table shows the effect of Kaolin as additives on the optical parameters. The values of energy gap, E_o ,λ_o , decreased as the Kaolin content increase ,while the values of ε_∞ ,S_o , U_E, n(o) , M_{-1} ,M_{-3} were increased by increasing Kaolin percentage.

Table 1. Optical Parameters of PVA-Kaolin

Sample	E_d (eV)	E_o (eV)	E_g (eV)	ε_∞	n(o)	M_{-1}	M_{-3} eV^{-2}	S_o x1 0^{15} m^{-2}	l_o nm	U_E meV
Pure	51	8.160	4.08	7.250	2.69	6.25	0.094	1.226	69	570
2 %	49	7.795	3.89	7.329	2.70	6.32	0.104	1.500	61	555
4 %	49	7.550	3.77	7.490	2.737	6.49	0.114	1.530	60	625

Conclusion

PVA: Kaolin films have been successfully deposited by casting method. The results suggest that there is an inverse relation between optical energy gap and Urbach energy. The addition of Kaolin enhances the absorbance and reflects on the enhancement of the optical energy gap by decreasing its value. The value of l_o is very small compared to the values of l_o in semiconductors. This is the first trial to apply Wemple, DiDomenico model to this composite with successful results.

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