

which are associated to disorder and structural defects in the polymer matrix. Fig. 6b displays variation of $\ln \alpha$ against $h\nu$ of pure and doped PVA samples and a linear fit is carried out in the linear parts of the curves to estimate Urbach energy, (E_u) values. Urbach energy values are estimated and summarized in Table 1. It is found that, the values of E_u are increased with increasing the doping concentration until

certain concentration and then start to decrease again. The increase in the values of E_u suggested that the atomic structural disorder of PVA is affected by thiourea doping. This increase in E_u values leads to a redistribution of states, i.e., from band to tail, allowing a great number of possible transitions from the band to the tail and tail to tail [37].

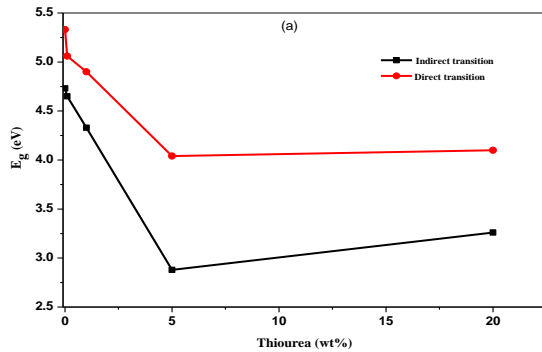


Fig. 6a: Values of optical energy gap versus thiourea wt%.

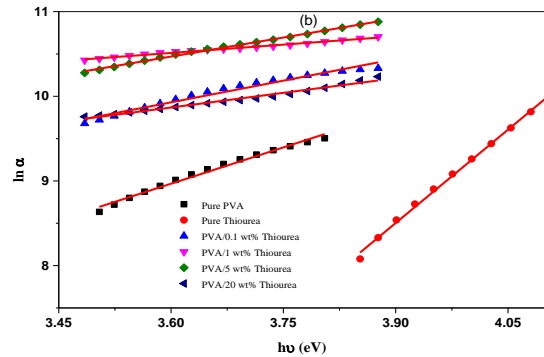


Fig. 6b: The variation of $\ln \alpha$ versus $h\nu$ for all samples.

Table 1: The values of absorbance edge, indirect and direct energy gap, Urbach energy, single oscillator energy (E_o) and dispersion energy (E_d) of all samples.

Sample	Absorbance edge (eV)	indirect energy gap, (eV)	direct energy gap, (eV)	Urbach energy (eV)	Single oscillator energy (E_o)	Dispersion energy (E_d)
Pure PVA	4.81	4.73	5.33	0.35	13.67	75.95
Pure Thiourea	3.93	3.84	4.37	0.14	4.27	1.94
0.1 wt % Thiourea	4.65	4.65	5.06	0.59	3.77	6.62
1 wt % Thiourea	4.36	4.33	4.90	1.53	4.31	33.14
5 wt % Thiourea	3.38	2.88	4.04	0.87	7.95	41.88
20 wt % Thiourea	3.62	3.26	4.10	0.67	7.25	34.50

Refractive index dispersion

The refractive index (n) can be estimated using the following

formula [38], $n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}}$, where R is the reflectance and

equals to, $R = 1 - \sqrt{T * \exp(A)}$ [36], where T and A are the transmittance and absorption, respectively. The variation of the refractive index for pure and doped PVA samples versus the wavelength is shown in Fig. 7a.

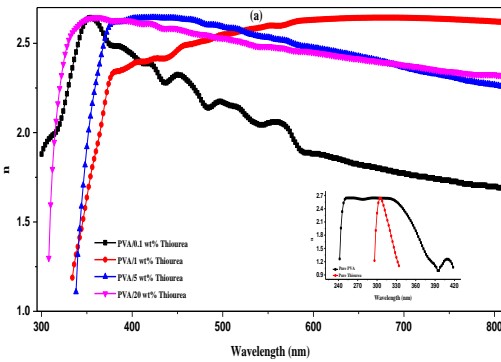


Fig. 7a: Refractive index versus the wavelength of all samples.

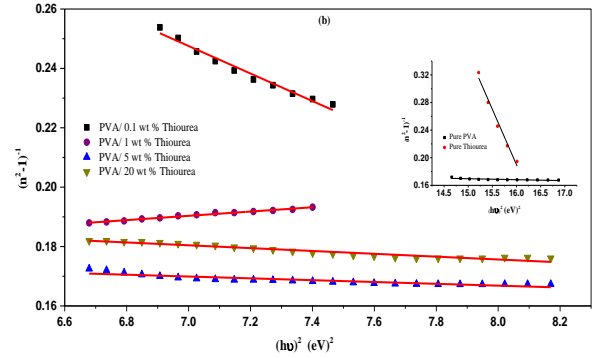


Fig. 7b: $(n^2-1)^{-1}$ versus $(hv)^2$ of all samples.

The dispersion has an effective role in detecting optical materials, because it is an important parameter in design of spectroscopic and optical communication devices. The dispersion of refractive index is attributed to the photon energy $E(\nu)$ according to the single-oscillator model which explains dielectric response of transitions under the interband absorption edge, as follows [39]

$$n^2 - 1 = \frac{E_o E_d}{E_o - (h\nu)^2} \quad (3)$$

Where E_o and E_d are defined as the average excitation energy of the electronic transitions and the dispersion energy, respectively. E_o is associated with the optical band gap and E_d is considered as a measure of average strength of the interband optical transitions. E_d is attributed to the distribution of the charges in the unit cell and depends on the chemical bonding [40]. Fig. 7b shows the variation of $(n^2-1)^{-1}$ against $(h\nu)^2$ for pure and doped samples. Values of E_o and E_d are calculated by knowing the intercept and slope of the Fig. 7b, and listed in Table 1.

The values of E_d and E_o are used to determine both static refractive index, n_o , and static dielectric constant, ϵ_s , based on the following equation [38]

$$n_o^2 = 1 + \frac{E_d}{E_o} \quad (4)$$

$$\epsilon_s = n_o^2$$

The relation between refractive index (n) and lattice dielectric constant (ϵ_L) can be expressed as follow [39]

$$n^2 = \epsilon_L - \frac{e^2}{\pi c^2} \left(\frac{Y}{m^*} \right) \lambda^2 \quad (5)$$

Where, e , c , (Y/m^*) and λ are the electronic charge, speed of light, ratio of carrier concentration to effective mass and wavelength, respectively. Fig. 8 shows the variation of n^2 versus λ^2 . The values of (Y/m^*) and (ϵ_L) are calculated by knowing slope and the intercept of Fig. 8 and summarized in Table 2. The difference between static and lattice dielectric constants values may be due to the contribution of free carriers in the different samples.

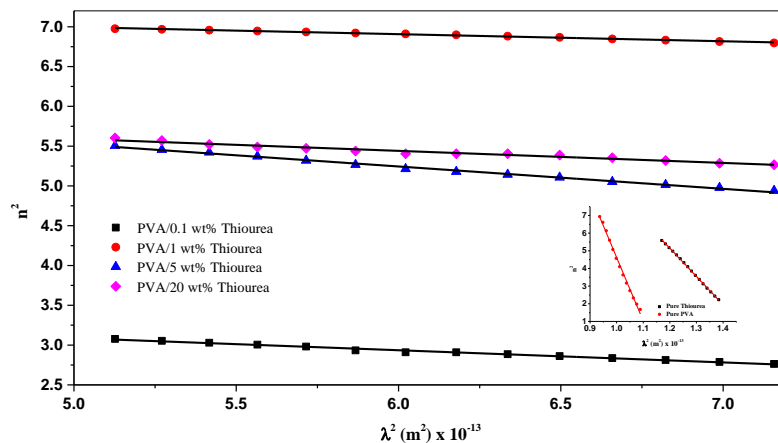


Fig. 8: The variation of n^2 versus λ^2 for all samples.

It is already well known that, the dielectric constant in the range of transparency can be written as follows;

$$n^2 = \epsilon_L - \frac{\omega_p^2}{\omega^2} \quad (6)$$

and

$$\omega_p^2 = \frac{e^2 \cdot \left(\frac{Y}{m^*} \right)}{\epsilon_0} \quad (7)$$

Where, ω_p , ω , e and ϵ_0 are defined as plasma frequency, frequency of the incident light, electron charge and permittivity of free space (8.854×10^{-12} F/m), respectively. The values of plasma frequency of the investigated samples are estimated and listed in Table. 2.

Table 2: Values of static refractive index, n_o , static dielectric constant, ϵ_s , lattice dielectric constant, ϵ_L and Y/m^* of all samples.

Sample	Static refractive index, n_o	Static dielectric constant, ϵ_s	Lattice dielectric constant, ϵ_L	Y/m^* ($10^{41} \text{ m}^{-3} \text{ g}^{-1}$)	Plasma frequency, ω_p (Hz)
Pure PVA	2.56	6.56	15.96	176	2.26×10^8
Pure Thiourea	1.21	1.45	35.95	396	3.38×10^8
0.1 wt % Thiourea	1.66	2.76	3.87	1.71	2.22×10^7
1 wt % Thiourea	2.95	8.69	7.42	0.95	1.65×10^7
5 wt % Thiourea	2.50	6.27	6.90	3.06	2.97×10^7
20 wt % Thiourea	2.40	5.76	6.36	1.70	2.21×10^7

CONCLUSION

Structure and optical properties of thiourea-PVA composites have been examined using different techniques such as, XRD, FTIR, Raman spectroscopy and UV-Vis spectroscopy. XRD results showed that thiourea is highly crystalline material with an intense sharp peak at $2\theta=20.98^\circ$ and the crystallinity of thiourea doped PVA samples increased with increasing the thiourea content. FTIR and Raman spectroscopy are used to investigate the change in the molecular structure. The analysis of UV-Vis data revealed that, values of absorption edge, direct and indirect optical gap energy are decreased with doping thiourea salt until a concentration of 5wt% and then start to increase again. Moreover, values of dispersion energy (E_d) and single oscillator energy (E_o) have been changed with the thiourea concentration as observed for direct and indirect optical energy. This behavior has been interpreted based on the aggregation of the thiourea dopant in the PVA polymer matrix. Static and lattice dielectric constants have been estimated.

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