

Structural and Optical Characterization of Thiourea-Poly (Vinyl Alcohol) Composites

T. Fahmy^{*1,2}, A. sarhan² and Z. M. Elqahtani³

¹Dept. of Physics, College of Science and Humanities in Al-Kharj, Prince Sattam bin Abdulaziz University, Al-Kharj 11942, Saudi Arabia.

²Polymer Research Group, Dept. of Physics, Faculty of Science, Mansoura University, 35516 Mansoura, Egypt.

³Dept. of Physics, College of Science, Princes Nourah bint Abdulrahman University, Riyadh, Saudi Arabia.

<https://orcid.org/0000-0002-5078-2245>

* Corresponding author

Abstract

The present manuscript reports the effect of thiourea doping on the optical properties of poly (vinyl alcohol), PVA. Films of thiourea doped PVA samples have been prepared using casting method. Different techniques such as, XRD, FTIR, Raman spectroscopy and UV-Vis spectroscopy have been used to investigate the prepared samples. XRD results show that thiourea is highly crystalline material with an intense sharp peak at $2\theta=20.69^\circ$ 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 PVA-thiourea composites. The optical constants of thiourea doped PVA samples have been estimated using the analysis of UV-Vis data. It is found 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. Values of dispersion energy (E_d), single oscillator energy (E_o) and different parameters of dielectric constant have been estimated.

Keywords: PVA, Thiourea, Optical gap, dispersion energy, single oscillator energy, Lattice dielectric constant.

INTRODUCTION

Polyvinyl alcohol, (PVA) is characterized by carbon chain backbone linked with hydroxyl groups. The hydroxyl groups, OH groups, are considered as a source of hydrogen bonding, therefore, it helps to form the polymer blends or polymer complexes [1-4]. PVA is water-soluble and biocompatible polymer and is vastly used in the preparation of polymer blends due to its excellent physical and chemical properties [5]. So the applications of PVA can be increased more and more by adding different dopant materials into PVA matrix [6].

Thiourea is considered as an interesting inorganic modifier matrix because of its higher polarity and its ability to compose an extensive hydrogen bonds network [7]. Thiourea crystals also show the piezoelectric effect and it is an organic nonlinear optical material and can be used in many applications, such as, frequency conversion, harmonic

generators, dynamic holography, frequency mixing, light modulation and optical memory storage [8,9].

The optical and electrical properties of polymer blends and polymer composites have been studied intensively [10-15]. The investigation of optical absorption spectrum of solids gives more details about both optical energy gap as well as the band structure of amorphous and crystalline materials. Information about atomic vibration and electronic states can be obtained by the analysis of absorption spectrum in the lower energy and higher energy regions, respectively [16-19]. In this manuscript, the effect of thiourea dopant on the structure and optical properties of PVA has been investigated.

EXPERIMENTAL WORK

Materials

Poly (vinyl alcohol) (PVA) is a commercial product, purchased from Merck, (Germany), with molecular weight equals to 72000 and thiourea salt after recrystallization, $M_w=76.12$, are supplied by BDH Chemicals Ltd, Poole, (England) and El-Nasr Co., (Egypt), respectively.

Sample Preparation

Doped PVA samples with different ratio of thiourea are prepared using casting method. PVA and thiourea are dissolved in distilled water for few hours at $T = 343$ K. The solution is continuously stirred for two hours to get a homogeneous mixture. The solution is then casted in petri dish in an oven regulated at $T = 343$ K for few days.

X-ray diffraction pattern of all samples is carried out using Rigaku Ultima IV diffractometer with Cu-K α radiation, ($\lambda = 1.5418$ Å at 40 kV), (at Central Lab, College of Science, Prince Sattam bin Abdulaziz Uni, KSA). FT-IR spectra are carried out between 400 and 4000 cm^{-1} by FT-IR spectroscopy, Mattson, UK (at Chemistry Dept., Faculty of Sci., Mansoura Uni. Egypt). Raman Spectroscopy is performed in the range 3650-50 cm^{-1} using Senterra II, Bruker (at Central Lab, College of Science, Prince Sattam bin Abdulaziz Uni, KSA). UV-Vis spectra are recorded between 200 and 800 nm using UV/Vis Unicam, Mattson, UK (at Chemistry Dept., Faculty of Sci., Mansoura Uni. Egypt).

RESULTS AND DISCUSSION

XRD

X-ray diffraction study of polymer and polymer composite is useful technique to investigate the amorphous and crystalline nature of the materials. Fig. 1 represents XRD spectrum of thiourea and thiourea doped PVA samples. The reflection peaks of thiourea are detected at 2θ , 20.69, 23.29, 28.51, 29, 31.41, 5.53, 42.33, 47.16, 48.86 and 51.66° , as shown in Fig. 1a. These reflections are consistent with characteristic peaks of the typical thiourea salt [20]. Fig. 1b displays XRD spectra of PVA and doped PVA samples with different concentrations of thiourea salt. It is found that XRD of pure PVA is

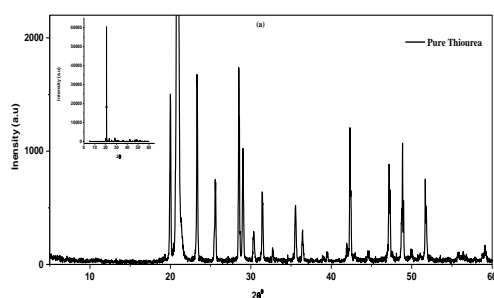


Fig. 1a: XRD spectrum of pure Thiourea.

characterized by a semicrystalline peak at $2\theta = 19.89^\circ$, as reported elsewhere, [21]. The intensity and position of this peak is changed with doping, indicating that the crystallinity of doped PVA samples has been enhanced. One can see that, highly doped PVA sample is characterized by an amorphous halo at $2\theta = 9.15^\circ$ and many reflection peaks at $2\theta = 20.18, 20.98, 23.42, 25.63, 28.58, 29.11, 31.43, 35.66$ and 36.41° . The higher degree of crystallinity depends mainly on the regular arrangement of molecules of the materials. Such behavior has been reported previously, thiourea may enhance effective delocalization of PVA chains leading to the ordering of polymer chains of PVA along the thiourea chains [22,23].

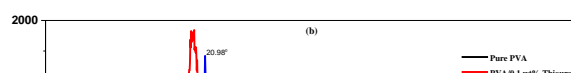


Fig. 1b: XRD spectra of PVA and doped PVA with varying thiourea concentrations.

FTIR-Spectroscopy

FTIR spectroscopy is useful to define the functional groups and to investigate the interactions and complexation in the polymeric materials. Fig. 2 displays FTIR spectra of PVA and thiourea doped PVA samples in the wavenumber region from 4000 to 400 cm^{-1} . It is observed that, FTIR spectrum of PVA, Fig. 2a, is characterized by many absorption bands, such as, the absorption bands in the range of 3400-3235 cm^{-1} are assigned to OH intermolecular hydrogen bonded. The absorption bands at 1720 cm^{-1} , 1564 cm^{-1} and 1427 cm^{-1} are attributed to and C=O stretching, C-H bending of CH_2 and -COO- stretching vibrations, respectively. The bands at 1333, 1250 and 1092 cm^{-1} are due to the interaction between O-H bending and C-O stretching. The bands at 916 and 848 cm^{-1} provide more information on the ratio of syndiotactic and

isotactic sequences in PVA matrix [24].

On the other hand, Fig. 2e shows FTIR of pure thiourea with characteristic absorption bands. The bands at 3378 cm^{-1} , 3269 cm^{-1} and 3172 cm^{-1} are attributed to different types of asymmetric and symmetric stretching NH_2 groups. Absorption bands at 2667 cm^{-1} , 2353 cm^{-1} and 2104 cm^{-1} are attributed to ammonium and iminium salt like structure. The band at 1617 cm^{-1} is attributed to thioamide ($\text{C}=\text{S}$ linked to nitrogen), asymmetric stretching vibration, whereas, the band at 1469 cm^{-1} is assigned to antisymmetric (NCN) stretching of the thiourea [25]. The absorption bands at 1087 cm^{-1} , 729 cm^{-1} , 632 cm^{-1} and 492 cm^{-1} are assigned to C-N symmetric stretching vibrations, C=S symmetric stretching vibrations, C-N bending vibration and $\text{N}=\text{C}=\text{N}$ rocking mode, respectively [26].

Fig. 2: FTIR spectrum of (a) pure PVA, (b-d) doped samples and (e) pure Thiourea.

Figs. (2b-d) display FTIR of thiourea doped PVA samples to investigate the local bonding structure in PVA. These bonds are affected after doping the polymer structure of PVA with thiourea salt. The strong hydrogen bonding between both PVA and thiourea salt leads to the absorption bands to become sharper and shifted to higher frequencies in the range of 3300-3500 cm^{-1} . The band at 1720 cm^{-1} (C=O) of PVA has been shifted to lower wavenumber $\sim 1702 \text{ cm}^{-1}$. The absorption band at 1092 cm^{-1} which is measured the crystallinity degree of pure PVA is shifted to higher wavenumber at 1127 cm^{-1} . The shift in the band positions to higher frequency values can be ascribed to greater double bond character of C=N during the formation of PVA-thiourea complex [20]. Moreover, some of absorption bands having different intensities and positions are detected which are attributed to different bending and stretching vibrations, such as, 2937 cm^{-1} , 1564 cm^{-1} , 1333 cm^{-1} and 848 cm^{-1} , respectively

Raman Spectroscopy

Raman spectroscopy is a non-destructive technique to characterize the crystalline materials. It is intensively used to define functional groups for knowing the molecular structure of polymer complexes and composites and it can be used also in conformational analysis of samples. In general, chemical bonds containing heavy atoms show an intense Raman band compared to those containing lighter atoms. Hence, the Raman scattering intensity produced by the double bond vibration is much stronger than that produced by single bond vibration [27]. Fig. 3 displays Raman spectrum of PVA/0.5 wt% thiourea, as a representative sample of doped samples in the 50-3500 cm^{-1} region.

Fig. 3: Raman spectrum of PVA/0.5 wt% thiourea.

The main characteristic Raman bands of thiourea have been observed at 1371, 1094, 733 and 486 cm^{-1} . These bands are assigned to N-C-N symmetric stretching modes, strong coupling of C-N stretching with the NH_2 group rocking, C-S stretching and N-C-N bending, respectively. On the other hand, because of the low polarizability and low intensity, SCNN out-of-plane bending mode can't be observed in this present Raman spectrum, but it is found at $\sim 632 \text{ cm}^{-1}$ in FTIR spectrum of thiourea, as shown in Fig. 2e [28]. A broad band has been observed at 3278 cm^{-1} and is raised from OH stretching, indicating that the presence of hydroxyl groups. The band with a maximum at 2912 cm^{-1} is related to the vibrations of valence C-H, whereas, the band at 1371 cm^{-1} is attributed to the vibrations of valence C-O of secondary alcohol. The region 1200–1000 cm^{-1} consists of different numbers of modes are sensitive to the crystallinity degree in PVA [29]. The bands at 924 cm^{-1} , 856 cm^{-1} and 418 cm^{-1} are attributed to twist mode of syndiotactic, isotactic sequences and C-H out of plane vibration, respectively [30].

UV-Vis Spectra

UV-Vis spectroscopy of PVA/thiourea composite samples have been investigated between 200 and 800 nm. PVA spectrum is characterized by three bands at 278, 313 and 410 nm, as observed in Fig. 4. The band at 278 nm is related to the absorption of carbonyl group (C=O), while, band at 313 nm is related to $-\text{CO}-(\text{C}=\text{C})_3$ -group [31,4]. UV spectrum of pure thiourea salt has been characterized by three bands at 237, 270 and 350 nm, respectively. The band at 270 nm which is observed as a shoulder is attributed to $n \rightarrow \pi^*$ transition, whereas, the band at 350 nm is related to $\pi \rightarrow \pi^*$ transitions of the thiocarbonyl group [32]. The wide range of transparency of absorption spectrum of thiourea salt in the visible range as well as the lower value of cut-off wavelength indicates the possibility of using thiourea salt in many applications in the field of higher harmonic generation and optoelectronic applications [33]. On doping with thiourea, UV absorption spectrum of pure PVA has been altered, as represented in Fig. 4a.

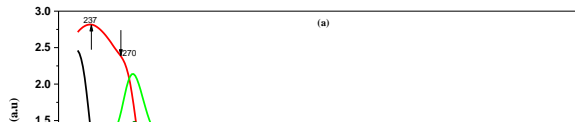


Fig. 4a: The absorbance versus the wavelength for all samples.

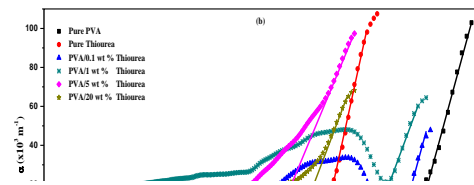


Fig. 4b: The absorbance coefficient versus the photon energy for all samples.

The absorption coefficient (α) is calculated using the formula,

$$\alpha = 2.303 \frac{A}{d}, \text{ where, } A \text{ is the absorbance and } d \text{ is sample}$$

thickness, respectively. Fig. 4b shows the relation between the absorbance coefficient and photon energy for all samples. The values of absorption edge are determined for the samples by extrapolating the linear portion of α against $h\nu$, as shown in Fig. 4b, to zero absorption value, and listed in Table 1.

The absorption spectra measurement is considered the simplest way to investigate the band structure of the materials. During the absorption process the electrons are stimulated from a state of lower energy to state of higher energy by absorbing a photon of energy known in the transmitting radiation. Hence, changes in transmitted radiation can identify the possible types of electronic transitions. Absorption coefficient (α) for amorphous and semiconductors can be expressed as follows [34]

$$\alpha = B \frac{(h\nu - E_g)^n}{h\nu} \quad (1)$$

Where, B , $h\nu$, E_g and n are constant, photon energy, optical

band gap energy and an exponent, respectively. The exponent n depends mainly on the transition nature and is relevant to density of states distribution. For direct allowed transitions, n equals to $1/2$ or $3/2$, whereas, for indirect forbidden transition n equals to 2 or 3. It is reported previously, near the edge of fundamental band the indirect and direct transitions is obtained and observed by plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ against photon energy ($h\nu$) [35]. Fig. 5a&b displays the variation of $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ versus ($h\nu$) to estimate indirect and direct optical gap energy values which are summarized in Table 1. It is found that, values of absorption edge, direct and indirect optical gap energy are decreased with doping thiourea salt until a concentration of 5wt%. For further increasing in doping concentration, these values begin to increase again, as displayed in Fig. 6a. This behavior revealed that, position of the electronic band gap of the doped samples depends mainly on the doping concentration of thiourea. When the dopant concentration is increased, it led to an aggregation of the dopant in the polymer matrix. These aggregations resist the motion of the charge carriers resulting in higher value of optical band gap energy.

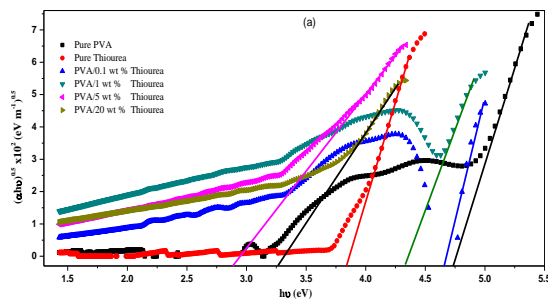


Fig. 5a: $(\alpha h\nu)^{0.5}$ versus $(h\nu)$ of all samples.

Fig. 5b: $(\alpha h\nu)^2$ versus $(h\nu)$ of all samples.

In the range of low photon energy and near the fundamental absorption edge, it is assumed that, the absorption coefficient (α) is dependent exponentially on $h\nu$ and follows the empirical Urbach rule as follows [36]:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right) \quad (2)$$

Where, α_0 is a constant and E_u is the Urbach energy and denotes to the tail width of localized states in the band gap

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].

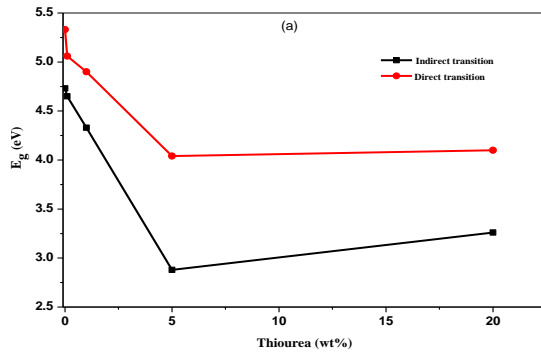


Fig. 6a: Values of optical energy gap versus thiourea wt%.

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, $R = 1 - \sqrt{T \cdot \exp(A)}$ [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 $(h\nu)^2$ 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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