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To cite this article: Mohammed Ghazi Hammed and Ahmed Abd Hassan 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **928** 072157

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Enhancement of the Structural and Optical Properties of (PVA-PANI) Polymer Blend By Addition of CuI Nanoparticles

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Abstract

PVA:PANI/CuI thin film composites have been prepared by adding (CuI) particles to the mixture of the poly vinyl alcohol (PVA) and conductive polyaniline (PANI) with various concentrations (0, 2, 4, 6, and 8% wt) using casting method technique on a glass substrate at laboratory temperature. The prepared thin film samples have lightweight, low cost, and flexible. The morphological, structural, and optical properties of these composites were examined by using Fourier transform - infrared spectroscopy (FTIR), X-ray diffraction (XRD), and Atomic Force Microscopy (AFM).

The effects of CuI concentrations on the optical properties of the PVA:PANI thin films were studied in the region of wavelength (190-1100) nm. The results are presented the prepared thin films have high values of absorption in UV range. Increasing CuI nanoparticle concentrations lead to increases the absorbance of (PVA:PANI) blend. The optical coefficients rise while the energy gap and transmittance falls with increasing CuI nanoparticle concentrations.

Keywords: *poly vinyl alcohol, polyaniline, CuI nanoparticle, polymer blend*

1- Introduction

Polymers have been drawn a massive attention in device manufacturing as a result of their incredible intrinsic properties such easy of fabrication, easy processability, lightweight, flexibility, and high mechanical strength. The use of polymers is a noticeable technique in production of semiconductor nanoparticles [1- 3]. Currently, the polymer blends are of massive attention due to their possible applications in the fields of desirable sizes, interfacial contacts, and thin film formation. The cause is that the polymer matrices allow processability because of solubility, low cost, growth's control, and morphology of the nanoparticles. Also, polymers are defined by the stability after the chemical and physical doping [4, 5]. There is widely growing in scientific and technological attention for polymeric composites because of their high application range offered by these hybrid composites. When inorganic particles are



implanted to polymers, it is estimated that its actions could be changed. Hence, it is possible to develop functions for these embedded polymers with unfamiliar properties because the role that the particles in semiconductors and metals could be successfully accommodated in polymers; ever since the polymers execute as surface capping agent when the particles are embedded into polymers [6, 7].

Various studies in the literature showed the efforts for preparing of the nanoparticles doped polymers, within the possibility of wide in the morphological structure and optical properties of its applications with highly optoelectronic performance, fuel cells, biomedical science, optical devices, and sensors [8, 9]. Principally, polymer/metal nanocomposites like polymer/Copper iodide nanoparticle composites are favorable effective materials in various fields [10].

Polyvinyl alcohol (PVA) is recognized among few vinyl polymers capable to dissolve in water is a solubilized crystalline structure polymer [11, 12]. Its repetitive unity is -CH₂-CHOH-, the alcohol group OH- is located on alternating carbon atoms. A source of hydrogen bonding is OH groups and hence contribute in the formation of polymer blends [13]. (PVA) has gotten a great attention because of its excellent charge storage capacity, high dielectric strength, and dopant reliant on the electrical properties either in the pure or mixed with extra materials [14, 15]. Polyvinyl alcohol is a commonly used thermoplastic polymer that is nontoxic and harmless. This is generally considered due to its use in cross-linked products and nanofillers [16]. Polyvinyl alcohol (PVA) is famous for its excellent transparency, low cost, good thermal stability, flexibility, nontoxicity, toughness, biodegradability, water solubility, and gas barrier properties. The optical applications of PVA are associated to the polarization, delay, and filtering of light, and the optical properties rely on the dopant [17, 18].

Through the last decades, conductive polymers have been the topic of various researches because of its outstanding optical properties initiating from its unique π -conjugated system along the polymeric backbone is responsible for high conductivity of PANI [19, 20]. Among the conducting polymers studied, polyaniline (PANI) is of particular interest due to their upcoming electrical conductivity, low cost, ease of synthesis, high environmental stability, interesting redox properties, simple doping/dedoping process, magnetoresistance (MR) behaviors, and electrochemical performances [21-23]. This resulted in its application to different fields, such as microelectronics, corrosion protection, sensors, and electrodes for batteries [24]. In evaluation with several scientific articles about PANI, researches on aniline are stay far away from sufficient due to the copolymer might overwhelmed the shortcomings of a single π -electron in the homopolymer, obtaining composites within outstanding property, studies on the copolymerization of aniline regularly attract people's interesting [25].

In this study, a trial will be carried out to produce and characterized the PVA:PANI/CuI nanocomposite using the casting method technique. The analysis will focus on the influence of concentration of CuI nanoparticles on the structure and the optical properties of the PVA:PANI thin films, using UV/Vis analysis, which gives a piece of evidence for understanding the effect of nanoparticles on the optical properties and energy band gap diagram on the host polymers.

2- Experimental part

Microscope glass slides were utilized as the substrate through the deposition process. The glass slides were first cleaned within an ethanol solution, then ultrasonically washed with distilled water. The polymers blend thin films of (PVA)- polyaniline (PANI), and copper iodide nanoparticles were blended by the casting technique. A (1

g) of PVA and PANI were melted in (30 ml) of distilled water. The weigh percent (50 wt% PVA, and 50 wt% PANI). The resulted solution was stirred to get a homogeneous solution at the constant temperature 325K for 12 hours. On the other hand, CuI nanoparticles were dissolved in double distilled water in the same condition and added to polymer blend with concentrations (2, 4, 6, and 8) wt%. The resulting solutions were cast to glass slides to get thin films of PVA:PANI and PVA:PANI/CuI, after that leave over it for about 72 hr. After drying, the thin films were kept in vacuum desiccators until use. The resulted samples were prepared with a thickness range (0.15–0.2) μm , the thickness was measured by a digital micrometer.

The absorption coefficient (α) of can be determined by [26]:

$$\alpha = (2.303A)/t \quad \text{----- (1)}$$

A and t refer to the absorbance and the thickness of sample respectively, while the non-direct transition model for (PVA:PEO/CuI) nanocomposites is described by:

$$ah\nu = B(h\nu - E_g)^r \quad \text{----- (2)}$$

where E_g refer to photon energy, B is constant. The relationship between the reflectance (R) and refractive index (n) is given by the equation [15]:

$$n = \frac{(1+R^{1/2})}{(1-R^{1/2})} \quad \text{----- (3)}$$

The extinction coefficient (k) is defined by the equation:

$$K = a\lambda/4\pi \quad \text{----- (4)}$$

The real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric constant of (PVA:PANI/CuI) thin films were calculated by using equations [27]:

$$\epsilon_1 = n^2 - K^2 \quad \text{----- (5)}$$

$$\epsilon_2 = 2nK \quad \text{----- (6)}$$

3- Results and Discussion.

3-1- Structure properties

3-1-1- FTIR test

FTIR spectroscopy has been utilized to evaluate the interactions among ions or atoms in PVA:PANI blend polymers and their thin films after adding CuI nanoparticles to polymer blend with concentrations (2, 4, 6, and 8) wt% which causes some changes in the vibrational modes and bands position. The spectra data were recorded from 4000 to 400 cm^{-1} . These interactions might induce changes in the vibrational modes of polymer blend and polymer composites of thin films under investigation. Figure (1) shown that some polymer chains have been formed and other chains have been broken [17]. In the spectrum of PVA:PANI characteristic bands are observed at 3450, 3215, 3120, 3029, 2945, 1641, 1602, 1568, 1492, 1402, and 1236 cm^{-1} . A band at 3450 cm^{-1} is assigned to the free N-H stretching vibrations of an amino group of PANI [28]. The broadband 3215 cm^{-1} matches to the O–H stretching vibration bend. The intensity of this band is due to PVA which contains O–H functional group [29, 30]. The band corresponding to C-H asymmetric stretching vibration occurs at 3120 cm^{-1} arising from aromatic C-H group of PANI and C-H symmetric stretching vibration at 2945 cm^{-1} arising from aliphatic C-H group of PVA [17, 31]. The C=C stretching vibration in the benzene ring can be linked with a strong band at 1641 cm^{-1} . The reached FTIR spectra in the current work is close to that informed in earlier studies [32]. The high frequency bands at 1568 and 1492 cm^{-1} were due to the presence of the benzenoid and

the quinold respectively [20, 33]. The peak at 1236 cm^{-1} is because C-N stretch of the aliphatic amine. Also, the strong peak at 1107 cm^{-1} relates to C-O stretching.

From the figure (1), the relative intensities of some characteristic vibrational bands for those CuI blends are decreased. This indicates that the amorphous regions of the prepared samples are augmented by increasing the CuI nanoparticles. The shifts of N-H stretching vibrations from 3450 cm^{-1} to 3431 cm^{-1} , C-H asymmetric bending from 3120 cm^{-1} to 3113 cm^{-1} , C-H symmetric stretching vibration from 2945 cm^{-1} to 2927 cm^{-1} , C=C stretching vibration from 1641 cm^{-1} to 1633 cm^{-1} , C-N stretch from 1236 cm^{-1} to 1184 cm^{-1} , and C-O stretching from 1107 cm^{-1} to 1103 cm^{-1} were observed. These indicate the chemical interactions of CuI with the polymer blend [5, 34]. The peak of vibrations are shown in Table 1.

Table (1): FTIR peaks of PVA:PANI/CuI polymer composite thin films.

Band assignments Pure	Wave number (cm^{-1})				
	0%	2%	4%	6%	8%
N-H stretching	3450	3458	3442	3442	3431
O-H stretching vibration	3215	3217	3234	3242	3230
C-H asymmetric stretching vibration	3120	3163	3051	3130	3113
C-H asymmetric stretching vibration (stander)	3029	3043	2962	2950	2927
C-H symmetric stretching vibration (bending)	2945	2950	2962	2950	2927
C=C stander	1641	1635	1633	1633	1633
N-H	1602	1602	1620	1620	1622
benzenold	1568	1583	1556	1568	1544
quinold	1492	1487	1512	1505	1508
C=C stretching vibration	1402	1402	1396	1396	1398
C-N stretching modes for benzoid ring	1236	1213	1288	1292	1184
C-O	1107	1097	1103	1180	1103

3-1-2- XRD test

The XRD is valuable technique to examine the crystallization and structure of the polymer matrices. Fig (2) illustrates the XRD patterns of PVA:PANI blend polymers and their thin film samples after adding CuI nanoparticles at room temperature in the range $0^\circ \leq 2\theta \leq 80^\circ$. It was gotten that the first reflection broad peak near 2θ at 20° displays the characteristic of crystalline and diffused in hallow amorphous phases of conventional semi-crystalline PVA in the PVA/PANI composite film. The semi-crystalline nature of PVA results from the strong intermolecular interaction between PVA chain through the intermolecular hydrogen bonding [10, 35, 36]. The crystalline peaks close to 2θ of 21° , 21.9° , and 23° in the XRD spectra of PVA/PANI composite film are attributed to the polymer chain of PANI [37]. This characteristic peak of PANI is ascribed to the periodicity perpendicular to the polyaniline chain. It is characteristic of van der Waals distances between stacks of phenylene rings (polyaniline rings) [35].

The high diffraction peaks at 2θ values of 26° , 42° , and 50° are related correspondingly to (111), (220) and (311) crystalline plans of (FCC) structure of CuI nanoparticles [38].

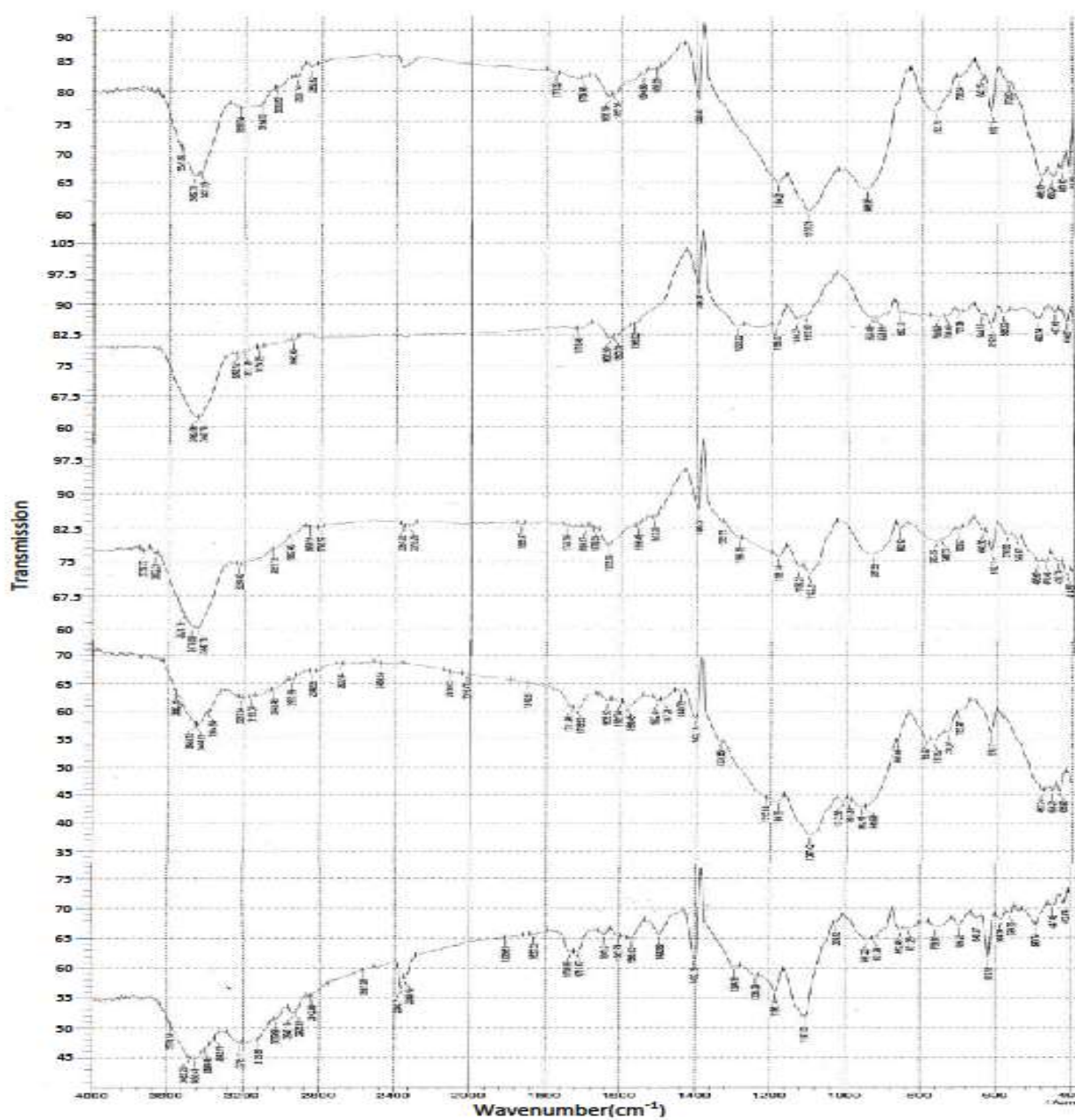


Figure (1) shown that some polymer chains have been formed and other chains have been broken [17]

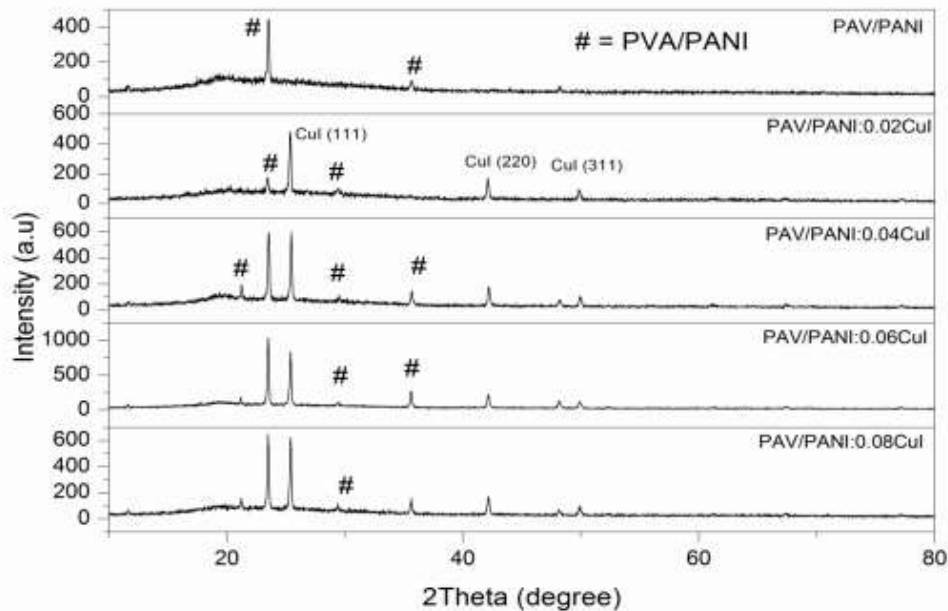


Figure (2) X-ray diffraction pattern of PVA:PANI blend polymers and their thin film samples after adding CuI nanoparticles.

By rising the concentration ratio of CuI nanoparticles, the number of peaks rises, and becomes stronger, demonstrating an enhancement in the crystallinity. This enhancement might be attributed to the recrystallization of the films, by the improvement of the rearrangement atoms in the thin film structure.

3-2- UV-Visible spectra

UV-visible spectroscopy is one of the techniques that used to evaluation the electronic absorption of conductive polymers that is valuable for investigating the oxidation and doping state of the polymer backbone. The optical absorption spectra of the PVA:PANI blends polymers and their thin film samples after adding CuI nanoparticles are shown in Figure (3). All the samples illustrate an absorption peak at wavelength of 300 nm ascribed to the ligand-centered charge transfer (LCCT) transitions ($\pi - \pi^*$). The absorbance was improved in the UV range [29, 39]. Also, the photon energy is sufficient to cooperate with atoms and the donor has an electrons level close to the conduction band at UV range. The procedure of the transition of an electron could be change when the transmitted and absorbed radiation changes. The detected absorbance in UV range was greater than that in visible and close to infrared regions, and the reason is photon energy is not enough to cooperate with atoms, so, transmitting of photons can be occurred [26].

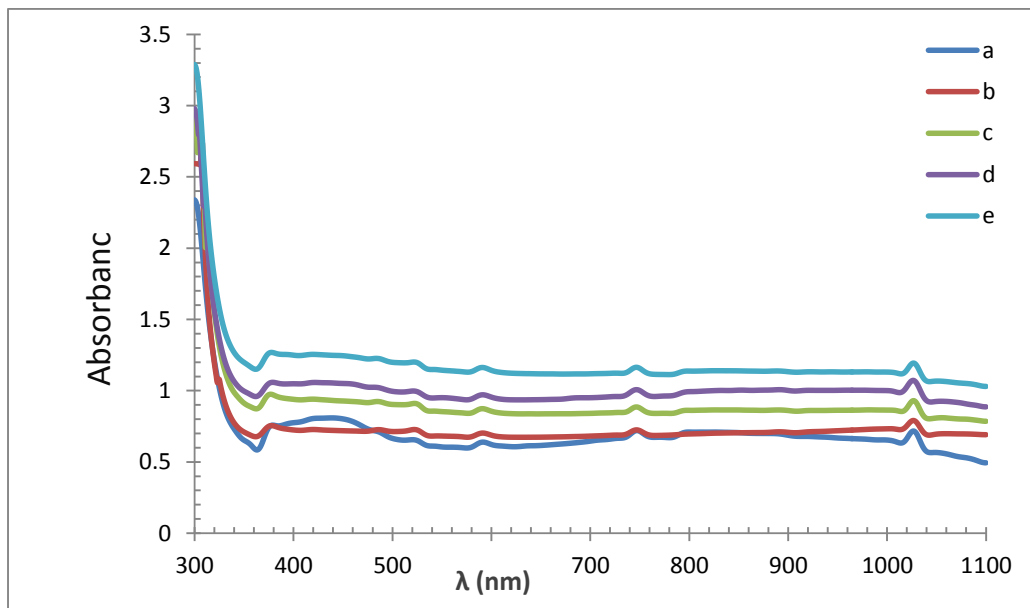


Figure (3): Optical the absorbance for thin films of (PVA:PANI/CuI) polymer composites with different concentrations of CuI . (a)- 0wt% (b)- 2wt% (c)- 4wt% (d)- 6wt% (e)- 8wt%

It can be noticed in figure (3), the absorption peak location is exaggerated by changing the concentration of CuI nanoparticles. Furthermore, the absorption edge differs with rising the concentration of CuI in PVA:PANI polymers blend, consequently, by the increase of the weight percentages of CuI nanoparticles. It is directly proportional to the absorbance according to Lambert Beer Law, and the reason for this is due to the increased focus within the same volume of solution which failed later so increasing the number of molecules that were to absorb the incident light, absorbance is increased. These results are in agreement with [4, 5].

The absorption coefficient (α) was calculated by using equation (1). Figure (4): shows the relation between the absorption coefficient and wavelength of the PVA:PANI/CuI polymer composites. The absorption coefficient improved with increasing the concentration of CuI nanoparticles, the change in the absorption coefficient was small at high wavelengths (low energies) and this shows a few possibility of electronic transitions. At low wavelength, the change of absorption coefficient was large and this shows the large possibility of electronic transitions is the absorption edge of the region.

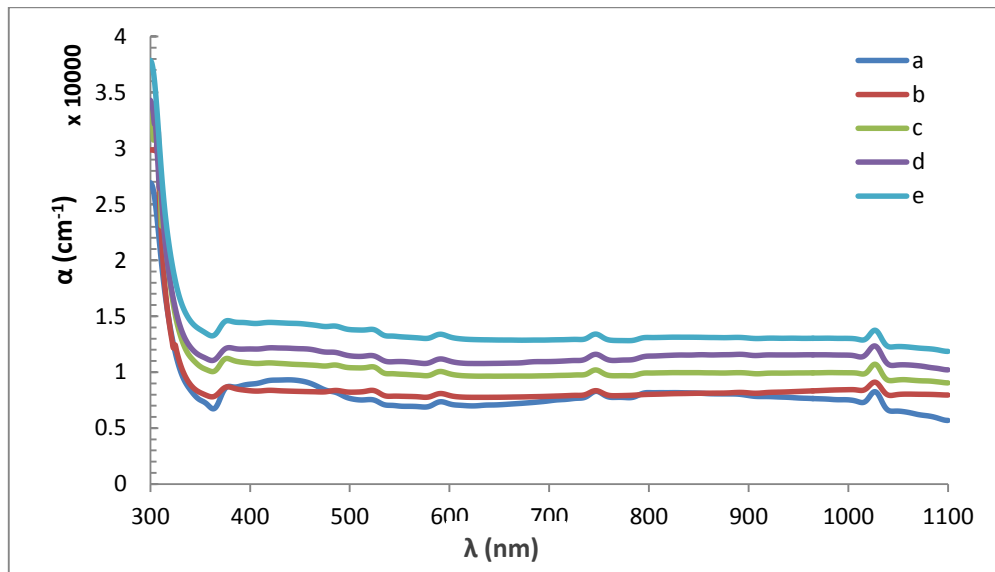


Figure (4) Absorption Coefficient (α) of PVA:PANI/CuI polymeric compounds at different concentrations (a) 0 wt%, (b) 2 wt%, (c) 4wt%, (d) 6 wt%, and (e) 8wt%.

The optical band gap energy of samples can be determined using equation (2), and deduced from the intercept of the extrapolated linear part of the plot of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ versus the photon energy $h\nu$ for direct and indirect transition band optical energy gap respectively of PVA:PANI/CuI thin films and their diagram was depicted in the figure (5). Furthermore, the direct energy gap values have been gotten by extrapolating the straight-line portion of the curve to the intercept of the energy axis at $\alpha=0$. The average value of E_g for these thin films found in the range of 3.75–3.9 eV for direct transitions as shown in table (2). It was seen from Figure (5) that the optical energy gap values of doped PVA:PANI are a smaller amount compared with the pure PVA:PANI. These variations in the Energy gap values of CuI doped PVA:PANI films certify the modifications in the PVA and PANI microstructures and band structure, due to the creation of additional groups for the optical transitions [40].

From figure (6) and table (2), it is clear that the indirect E_g values drop with rising in the CuI concentration in the polymer blend. The doped CuI salt rises the disorder of the polymer structure, which led to drop in the optical energy gap value. From all of the prepared samples, the 8 wt% CuI doped polymer blend displays the lowest direct and indirect energy gap values [14].

Table(2) Direct and indirect band gap values for pure and CuI doped (PVA:PANI/CuI) polymer blend thin films.

PVA:PANI/CuI	E_g (eV)	E_g (eV)
	Allowed direct	Allowed indirect
0	3.9	3.4
2%	3.86	3.35
4%	3.82	3.3
6%	3.8	3.28
8%	3.75	3.22

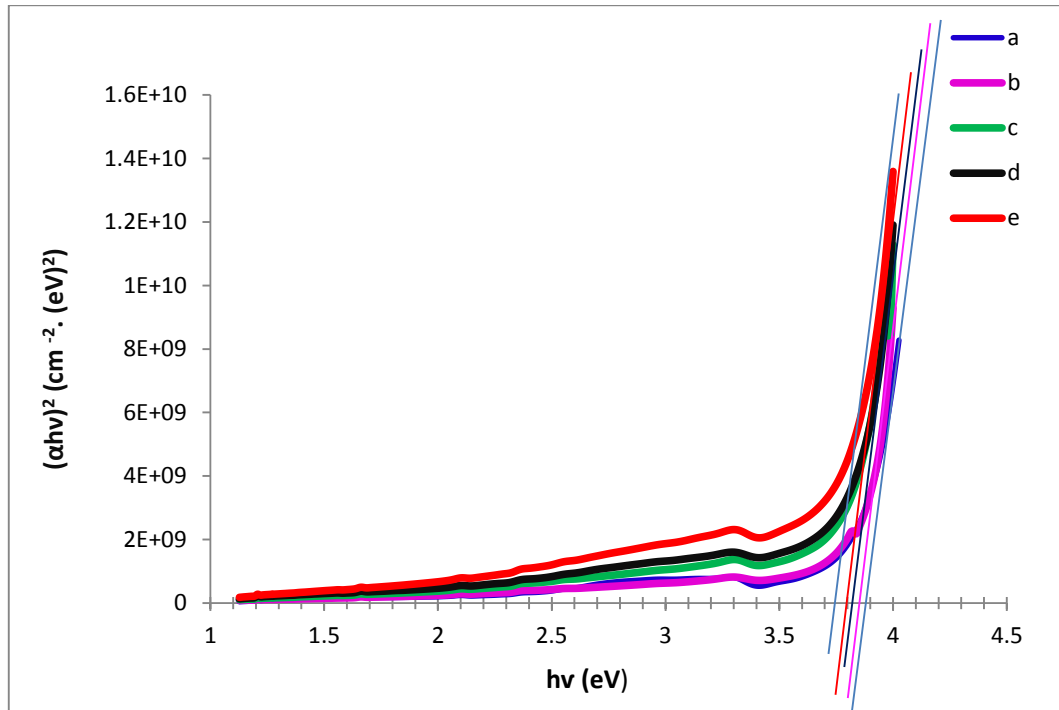


Figure (5) Graph of $(\alpha h\nu)^2$ versus photon energy for pure and CuI doped PVA:PANI polymer composite films at different concentrations (a) 0 wt%, (b) 2 wt%, (c) 4wt%, (d) 6 wt%, and (e) 8wt%.

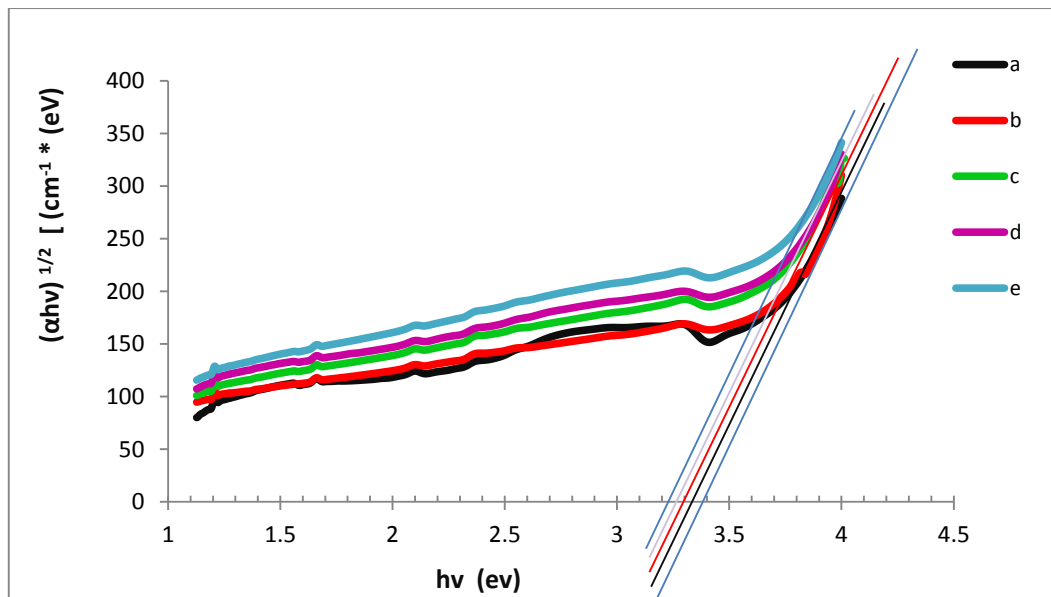


Figure (6) The plot of $(\alpha h\nu)^{1/2}$ versus photon energy for pure and CuI doped PVA:PANI polymer composite films at various concentrations (a) 0 wt%, (b) 2 wt%, (c) 4wt%, (d) 6 wt%, and (e) 8wt%.

Conclusions

From the gotten results and discussions one can conclude the following:

1. The FTIR spectrum peaks correspond to molecular vibrations and chemical bonds, indicate the presence of CuI in the PVA:PANI polymer structure.
2. Characterization using XRD show that CuI particles grew in PVA:PANI polymer matrix whereas the intensity of the peaks increases with increasing CuI.
3. The obtained optical parameters were found to be strongly affected by CuI contents. The absorption spectrum of PVA:PANI/CuI polymer composites are increased by increasing CuI concentration between 0 and 8 wt.% while the optical energy gap decrease whenever the CuI concentration increased.

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