

Effect of CuO Doped Polyvinyl Alcohol on the Structural and Optical Properties of PVA Films

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Abstract

The effect of copper oxide doped in PVA on the structural and optical properties of composite films is studied experimentally. Samples are PVA films of 20 ± 1 μm thickness doped with different studied using X – ray diffraction. Using the transmittance of samples, the effect of doped and their concentration on optical parameters of PVA films include absorption and others parameters. Results show the band gap energy of samples is decreased.

Keywords : PVA films, doping, optical properties.

Introduction

In the recent years, studies on the electrical and optical properties of polymer have attracted much attention in view of their application in electronic and optical devices. Electrical conduction in polymers has been studied aiming to understand the nature of the charge transport prevalent in these materials while the optical properties are aimed at achieving better reflection, antireflection , interference and polarization properties [1].

One of the important classes of polymer electrolytes is polar polymer like polyethylene oxide (PEO), polypropylene oxide (PPO), polyvinyl alcohol (PVA), ect. In this paper, We have used PVA as a host polymer because PVA is semi – crystalline polymer, good charge storage capacity, having high dielectric strength, flexible light weight materials and can be produced at a low cost [1-3]. Various composite materials have been recently synthesized by starting from different polymers and a wide variety of dopants like metals, oxides, inorganic salts and other particles. The incorporation of the dopants into polar organic polymers can induce pronounced changes in various properties of polymers in order to modify and improve its properties [4, 5]. In the present work is to investigate the structure and optical properties of polyvinyl alcohol (PVA) doped with varying concentration of copper oxide (CuO).

Experimental

A polyvinyl alcohol polymer (PVA) solution was prepared by adding deionized distilled water to solid PVA ($-\text{C}_2\text{H}_4\text{O}-$)_n (where n = 30,000 – 70, 000, average molecular weight) and then stirred by a magnetic stirrer at 30 °C for one hour, a solution of $\text{CuCl}_2\cdot\text{H}_2\text{O}$ was prepared by adding deionized distilled water to solid $\text{CuCl}_2\cdot\text{H}_2\text{O}$ and then stirred by a magnetic stirrer at room temperature for ½ h. Appropriate mixtures of PVA and $\text{CuCl}_2\cdot\text{H}_2\text{O}$ solution were mixed by a different concentration of (1.5%, 2.5%, 3.5% and 4.5%).

The solution was poured into flat glass dish. Homogenous films were obtained after drying in an oven for (1 h) at 50 °C .The film thickness was measured with the help of thickness gauge (indicating micrometer) and was found to be $20 \pm 1\mu\text{m}$. Absorbance and transmittance measurement were carried out using UV/VIS spectrometers in the wave length range (200 – 1100) nm. In order to investigate the structure of the polymer by X- ray diffraction studies were carried out using type 6000, wave length 1.5418 \AA .

Results and discussion

XRD spectrum of pure PVA polymer films and CuO doped PVA are shown in figures (1). The diffraction pattern of undoped PVA indicates a diffraction band at $2\theta = 19.4^\circ$. It is well known that the peaks at $2\theta < 20^\circ$ are due to crystalline nature of PVA polymer molecular, which may be as a result of strong inter molecular and intra molecular hydrogen bonding between the PVA chains [6,7]. The peaks at angles larger than 20° may be due

to impurities. No characteristic peak of CuO – doping was observed at percentage (1.5%, 2.5% and 3.5%), which may be due to less dopant percentage, but the peaks PVA at $2\Theta = 19.4^\circ$ in pure shift up by about 1.5 degree in PVA doped spacing values of the corresponding planes. The intensity of diffracted X – ray photons from films has been increased noticeably after the doping process. The doping CuO is effect at 4.5% percentage where anew peak at $2\Theta = 31.5^\circ$, that meaning we need to doping 4% and more to apparent peaks of CuO.

The average size of grains has been obtained from the X – ray diffraction pattern by use of the scherrers formula [8, 9]:

$$D = \frac{K\lambda}{\beta \cos\theta} \dots\dots\dots(1)$$

Where D is the grain size, K is a constant equal to 0.49, β is the full width at half maximum (FWHM) and λ is the wave length of the X – ray . The obtained average grain size value of nano particles is 4.5 nm . table (1) show values grain size and photo energy gap.

Optical absorption measurements are carried out in particulars to check the presence of the CuO from in the polymer matrix. Fig. (2) shows the transmittance spectrum in the rang (200 – 1100)nm, It is clear from this figure that transmittance spectra for all films increased with increasing wave length.

The transmittance changed after addition of CuO in the PVA samples, it is transmission intensity decreases with increasing CuO concentration, leads to a decrease in light scattering losses.

The optical absorption coefficient (α) of PVA films is very important because it provides in formation on the electronic band structure, the band tail and energy gap [10]. We used the following equation to determine the absorption coefficient [11]:

$$\alpha = \frac{2.303 A}{d} \dots\dots\dots(2)$$

Where A is the absorbance, d is the film thickness. Fig. (3) shows the dependence of the absorption coefficient on the photon energy for samples pure and samples with different impurity percentage. For all PVA samples one can observe a slight increase up to a proximately (4.5) eV for sample (3 a) and (3.5) eV for samples (3b, 3c, 3d, 3e) which may be attributed to electronic transition from the bonding molecular orbit. The observed increase of the absorption coefficient after exposure and with increase CuO concentration of PVA films can be attributed to the existence of more transitions from higher vibration levels of the ground state to higher sublevels of first excited singlet state [10].

The optical energy band gap is determined by translating the spectra into Tauc’s plots. To translate the absorption spectrum into Tauc’s plots, we use the frequency dependent absorption coefficient given by Mott and Devis [11]:

$$\alpha E = B(E - E_g)^r \dots\dots\dots(3)$$

Where B is a constant and the exponent (r) is an empirical index, which is equal to 2, 3, $\frac{1}{2}$ and $\frac{3}{2}$ depending on the nature of electronic transition responsible for the absorption. The plot of the product of absorption coefficient and photon energy $(\alpha hv)^2$ versus the photon energy hv at room temperature shows a linear behavior, which can be considered as an evidence for direct transition [12]. Extrapolation of the liner portion of this curve to a point $(\alpha hv)^2 = 0$ gives the optical energy band gap E_g for the PVA films with different doping concentration. Figure (4) show the band gap for PVA films pure and with CuO concentration. Here, the transition between the valence and conduction bands is assumed to be direct transition. The figure show that , the band gap decrease with the increase of the doping concentration. These the decrease in energy gap with increasing CuO concentration , can be understood by considering the mobility gap variation in the doped polymer. The calculated values of energy gap are listed in table (1) as in above for different concentration of PVA blend. Also this decrease in band gap may be attributed to the presence of unstructured defects, which increase the density of localized states in the band gap and consequently decrease the energy gap [13].

The refraction index n value provides the optical properties of the film and it is related by the following equation [14]:

$$n = \frac{(1+R)}{(1-R)} + \sqrt{\frac{4R}{1-R^2}} - K^2 \dots\dots\dots(4)$$

Where R is the reflectance and K is the extinction coefficient and absorption coefficient can be related by [15]

$$K = \frac{\alpha\lambda}{4\pi} \dots\dots\dots(5)$$

As shown from Fig. (5), the refractive index decreases as the wave length increase until 300 nm and then become nearly constant with increasing wave length, the value of refractive index within the constant range was varying from 1.4 – 1.5 as the doping percentage increase.

Fig. (6) shows the dependence of the extinction coefficient increase as the doping percentage increased,

this may be attributed to high absorption coefficient.

The real (ϵ_1) and imaginary (ϵ_2) values were calculated using the form [15] :

$$\epsilon_1 = 2nK \dots\dots\dots(6)$$

While ϵ_2 is mainly depends on the K values, which are related to the variation of absorption coefficient [15] :

$$\epsilon_2 = 2nK \dots\dots\dots(7)$$

It is found that ϵ_1 increases as the increase doping, while ϵ_2 is mainly depends on the K values, which are related to the variation of absorption coefficient. As shown in fig. (7) and (8) respectively.

Conclusions

PVA films and CuO doped were prepared by casting technique. The characterization using XRD demonstrated that the nano partical (3.6 – 4.9) nm grew in PVA polymer matrix whereas the degree of crystalline of PVA polymer increase with increasing CuO. The constant transparency in the visible and near IR region revealed that this polymer can be used as an optical window within this spectral region. The optical energy gap is reduced as the doping percentage increase.

Table (1) values energy gap and grin size at different copper oxide concentration.

PVA /CuO	Energy gap (eV)	Grin size (nm)
Pure PVA	5.6	4.9
1.5%	3.9	4.5
2.5%	4.0	4.0
3.5%	3.4	3.9
4.5%	3.6	3.6

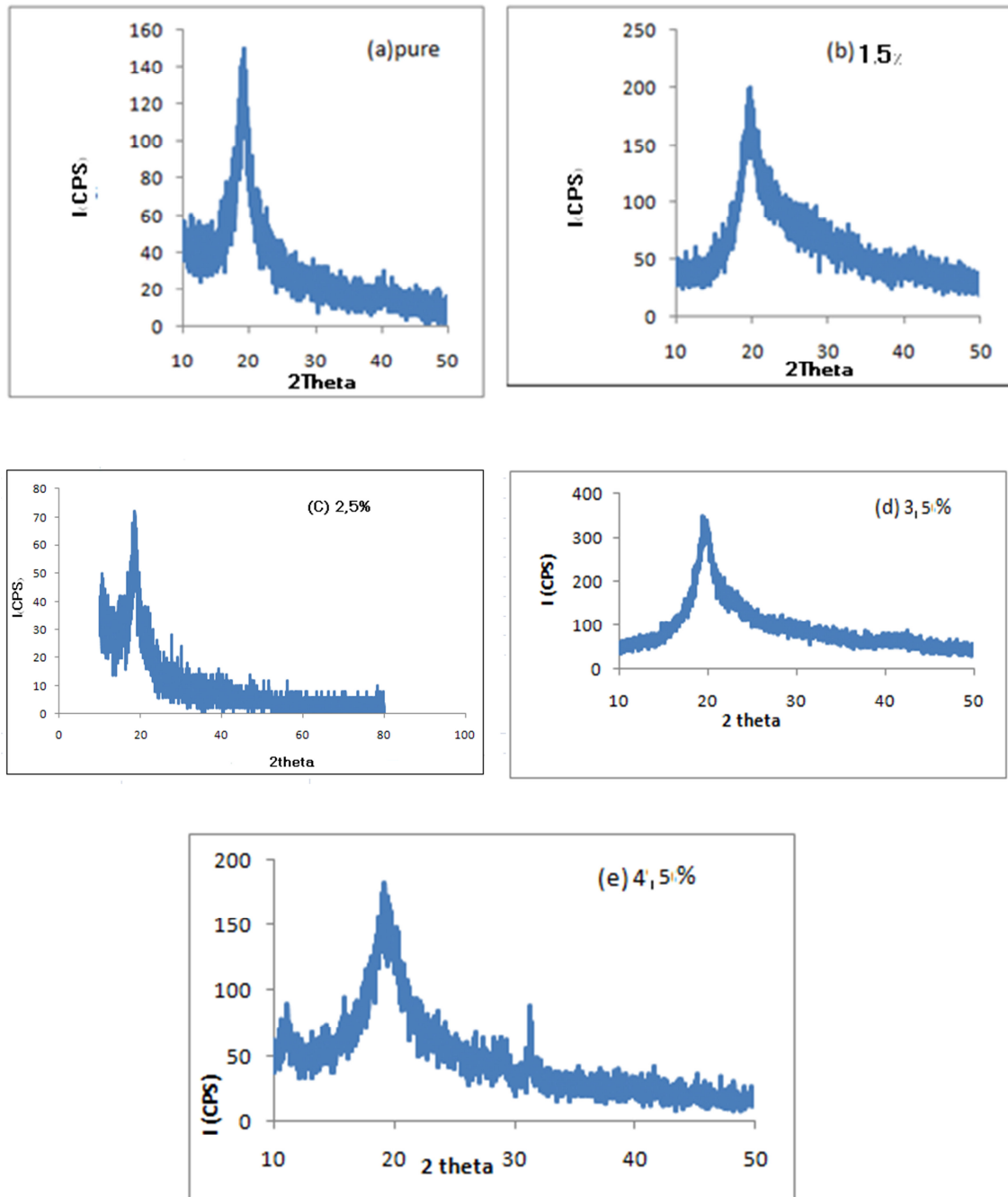


Fig. (1) X-Ray diffraction of PVA/ CuO films at different contrition.

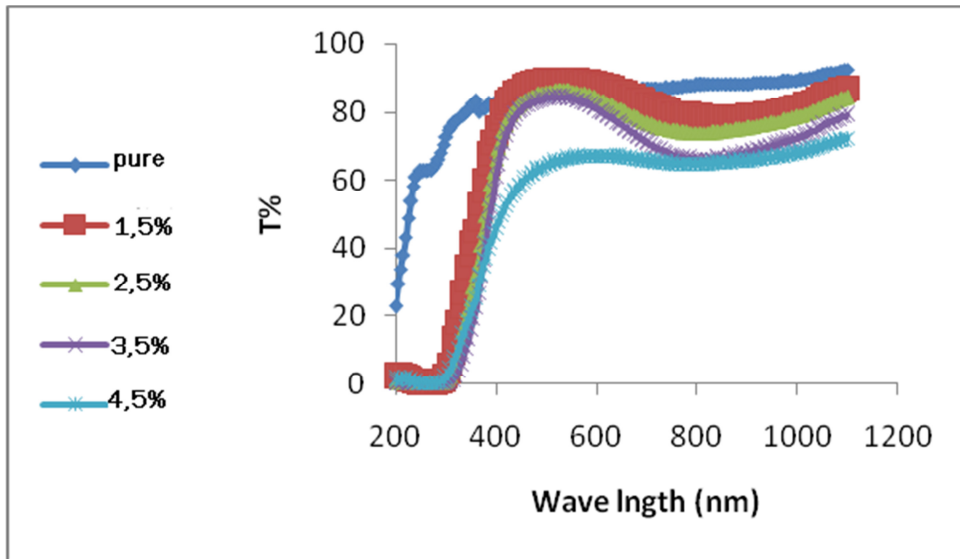


Fig. (2) transmittance of PVA / CuO at different concentration.

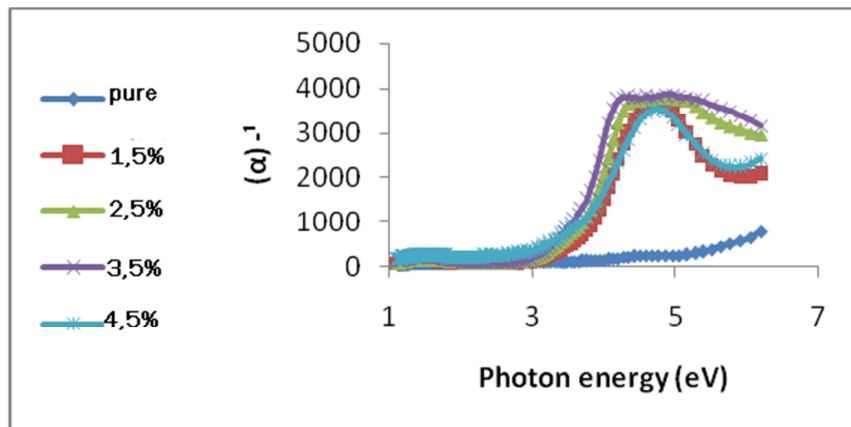


Fig. (3) Absorption coefficient of PVA / CuO films at different constriction.

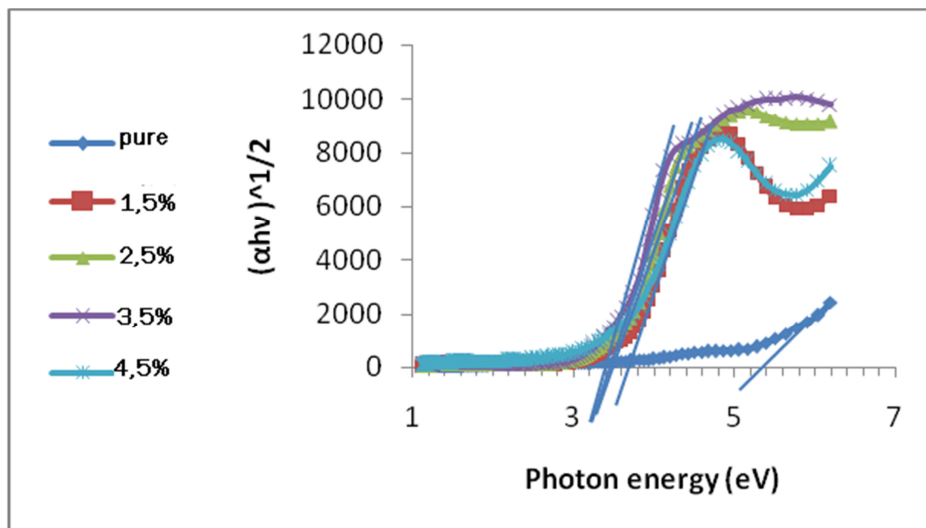


Fig. (4) optical energy gap of PVA/CuO films at different constriction.

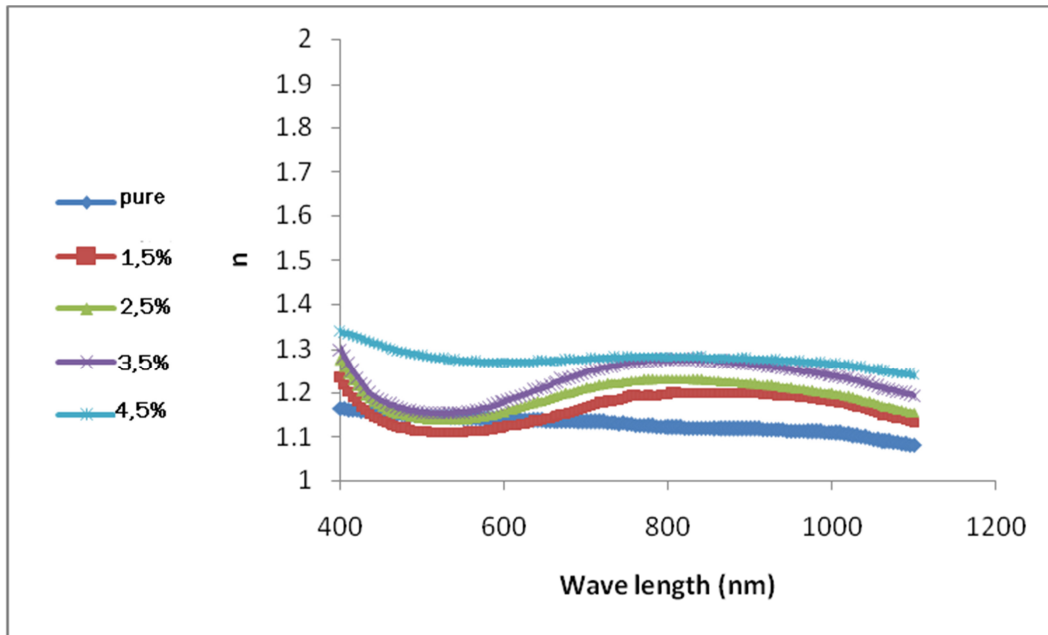


Fig. (5) Refraction index of PVA/CuO films at different concentration.

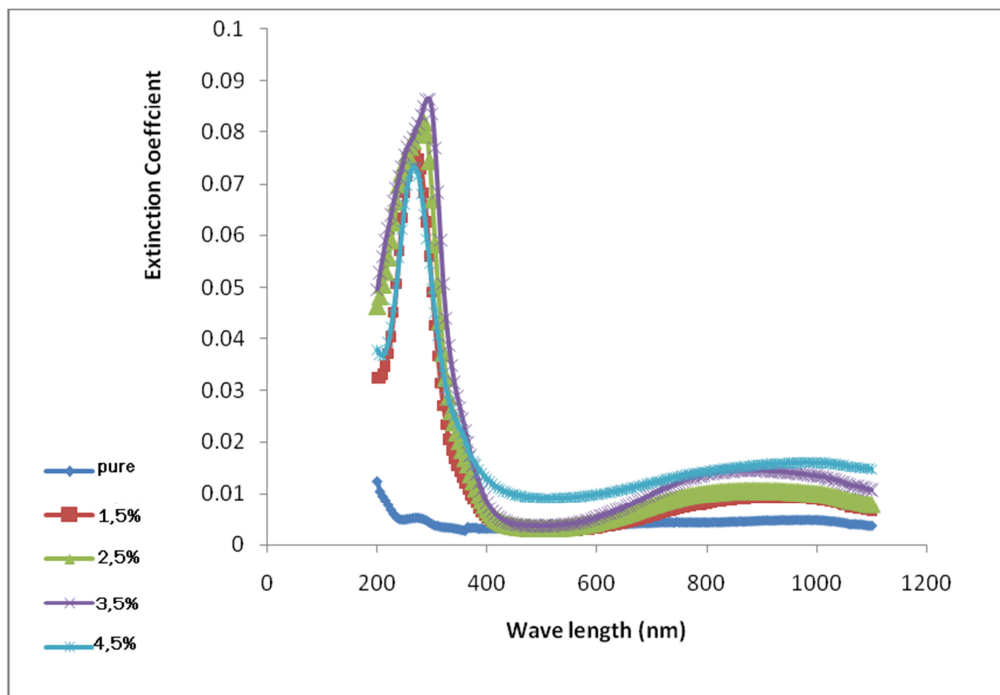


Fig. (6) Extinction Coefficient of PVA /CuO films at different concentration.

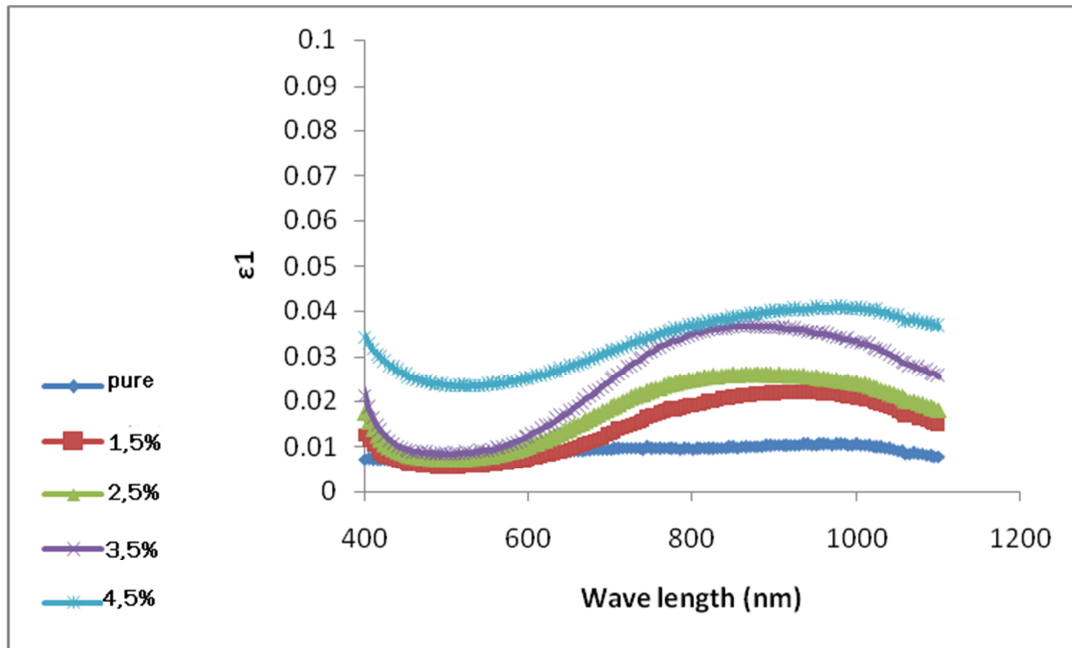


Fig. (7) Real Dielectric of PVA/CuO films at different concentration.

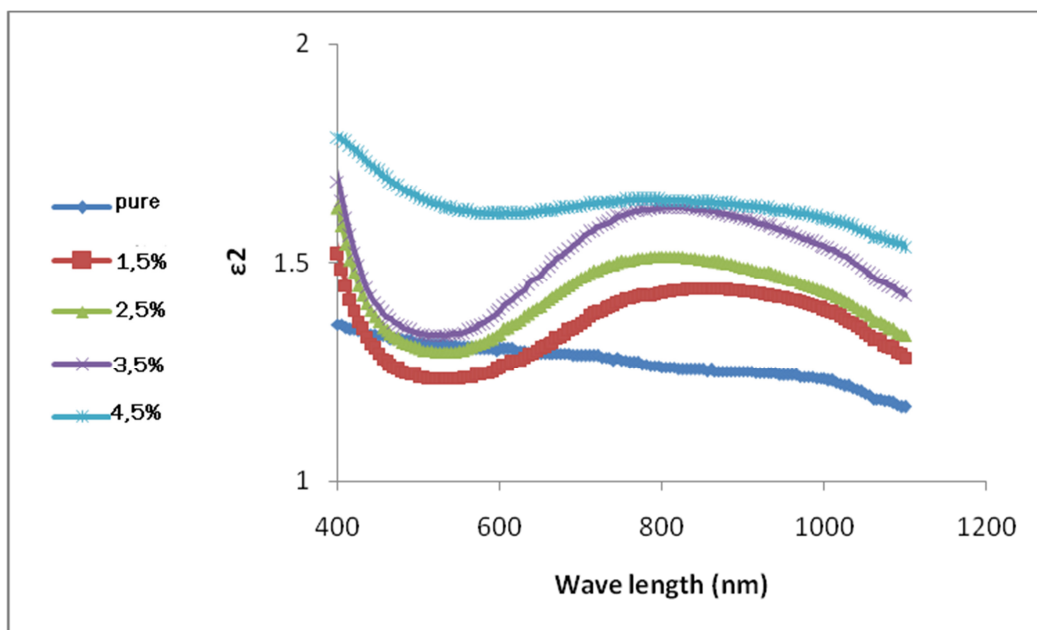


Fig. (8) Imaginary Dielectric of PVA/CuO films at different concentration.

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