

Study the Effect of Copper Chloride II (CuCl_2) on Optical Properties of Polyvinyl Alcohol (PVA)

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The optical properties of polyvinyl alcohol (PVA) doped with copper chloride II (CuCl_2) were studied. The copper chloride was added to polyvinyl alcohol with different concentrations (0, 1, 3, 5, 7, and 12 wt.%). The PVA: CuCl_2 films were prepared using the casting techniques. The absorption and transmission spectra have been recorded in the wavelength range (300-800) nm by using UV-VIS spectrophotometer. The fundamental optical parameters such as optical band gap energy, refractive index, extinction coefficient, and dielectric constants have been investigated. Results show that by adding copper chloride to PVA, the optical parameters (refractive index, extinction coefficient, real and imaginary dielectric constant) are increasing with the increase of concentrations of CuCl_2 . While the optical band gap energy decreases. The single oscillation energy E_0 and the dispersion energy E_d were determined by using the Wemple-DiDomenico model. The results show that E_0 and E_d values increase with increasing the dopant CuCl_2 concentration.

Keywords: Polyvinyl alcohol (PVA), casting techniques, optical constant, optical band gap, PVA: CuCl_2 films, Wemple-DiDomenico model.

1. Introduction

Composite materials are a material system composed of a combination of two or more materials that differ in form on material composition. The properties of a composite are different from those of its materials^{1,2}. It is also cohesive in structure. The composite comprises two major components: the matrix (the basic material) and the additives. The matrix is the basic material, serving to enclose the composite and give it bulk form. It surrounds other constituents and makes them more cohesive to form a "compact system". Additives are constituents added to polymers to provide them with specific properties and improve basic properties. These constituents are added in granular form or as small particles. Additives can increase the overall conductivity, reduce porosity, improve friction and some magnetic properties, etc³.

The study of the optical properties of polymers increases our knowledge of the type of polymer internal structure, nature of the bonds, and expands the potential scope of polymer application. Knowing the spectrums of absorbance and transmittance of a polymer assists in identifying many optical properties in different ranges of wavelengths. Conducting examination at the ultraviolet spectrum range enables us to know the type of bonds, orbitals, and energy beams. The study at the visible spectrum range provides sufficient information about the behavior of matter for solar applications. The study at the infrared range is very important in knowing the general structure of a polymer and the elements consisting of its chemical structure⁴.

Polyvinyl alcohol (PVA) based polymer electrolyte has attracted enormous attention in view of their satisfactory performance and biodegradability. PVA is a potential semi-crystalline polar polymer having an excellent charge storage capacity, high dielectric strength, good mechanical stability, and it has dopant-dependent optical and electrical properties^{5,6}. PVA has a carbon chain backbone with hydroxyl (O-H) groups that can be a source of hydrogen bonding, which assists the formation of polymer complexes and makes them as an excellent host material for solid polymer electrolytes (SPEs)⁷.

Poly (vinyl alcohol) (PVA) is the largest synthetic water soluble produced in the world. It is commercially produced by the hydrolysis of poly (vinyl acetate). The physical properties of poly (vinyl alcohol) depend on the method of preparation, as in the case of other polymers^{8,9}. The final properties are affected by the polymerization conditions of parent poly (vinyl acetate) used as well as the hydrolysis conditions, drying, and grinding.

Many research works carried on the effect of adding salt to polymers, and the optical properties of polymers electrolytic composites. For example, Hashim et al.¹⁰ studied the optical properties of PVA: CrCl_2 composites. The results showed that the absorbance increased with the increase in concentration of CrCl_2 , absorption coefficient, extinction coefficient, refractive index and real and imaginary parts of dielectric constants were increasing with increase in CrCl_2 concentration. Salman et al.¹¹ prepared and studied some electrical and optical properties of PVA: NiCl_2 composites. The experimental results for PVA: NiCl_2 films showed that the transmittance decreased with increasing

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the filler content, while the absorption coefficient increased with increasing the filler content. Moreover the results showed that it allowed indirect transitions, and the energy gap (E_g) decreased with increasing the filler content.

In the present work, the main goal is to investigate the effect of CuCl_2 on the optical properties of polyvinyl alcohol (PVA) films in the UV/VIS region, including the fundamental optical parameters such as optical band gap energy, refractive index, extinction coefficient, and dielectric constants. In particular, the introducing of an inorganic salt such as CuCl_2 into the polymer can improve and modify its optical properties, due to a strong interface interaction between an inorganic salt and the organic polymer. And another goal is to search for the possibility of obtaining the properties required to be appropriate for optoelectronic applications.

2. Experiment Work

2.1. Sample preparation

Films of Polyvinyl alcohol ($M_w = 72,000$) with copper chloride II (PVA: CuCl_2) were prepared by using the solution casting method. In this method, 1gm of pure PVA was dissolved in 50 ml of distilled water. CuCl_2 salt was also dissolved in 10 ml distilled water. The resulting blue-green color solution of CuCl_2 was added slowly to the polymer solution with different concentrations (0, 1, 3, 5, 7, and 12 wt.%). To obtain the complete dissolution, a magnetic stirrer was used at 333 K for 12 hours. These homogenous solutions were cast in a glass dish (diameter of 5 cm). The whole assembly was placed in a dust free chamber, and the solvent was allowed to evaporate slowly in open air at room temperature for 48 hours. The thickness of PVA: CuCl_2 films was measured using a digital micrometer screw gauge and found to be of the order of $65 \pm 01 \mu\text{m}$. It was determined at different places in each film. The transmission and absorption spectra of PVA: CuCl_2 films at room temperature have been recorded in the wavelength range (300-800) nm using the UV-VIS (Cary) spectrophotometer.

2.2. Theoretical background and basic equations

The optical absorbance spectra (A) of the PVA: CuCl_2 films were recorded in the wavelength range of 300-800 nm at room temperature by using UV-VIS spectrophotometer. The absorption coefficient $\alpha(\omega)$ was then calculated from the absorbance (A) by using the relation¹²:

$$\alpha(\omega) = \frac{2.303}{x} \log \left(\frac{I_0}{I} \right) = \frac{2.303}{x} A(\omega) \quad (1)$$

where I_0 and I are the incident and transmitted intensities of UV radiation, respectively, and x is the sample thickness.

A powerful method for determining the optical band gap energy is the plot of the absorption coefficient data with photon energy as:

$$\alpha \hbar \omega = \beta (\hbar \omega - E_{opt})^r \quad (2)$$

where, \hbar is Planck's constant, ω is the photon's frequency, E_{opt} is the optical band gap, and β is a proportionality constant^{13,14}.

The dependence of the absorption coefficient on the photon energy gives the nature of the optical transition by the value of the exponent r . It was found that for the tested composites ($r = 1/2$) for the direct allowed transition for electrons energy in k -space. Plotted $(\alpha \hbar \omega)^2$ versus photon energy ($\hbar \omega$), that obtain a good straight line, with extrapolation of the linear portion of these lines gives (E_{opt}).

At lower absorption coefficient level, in the range of $1-10^4 \text{ cm}^{-1}$, $\alpha(\omega)$ is described by the Urbach formula¹⁵:

$$\alpha(\omega) = \alpha_0 \exp (\hbar \omega / \Delta E) \quad (3)$$

where α_0 is a constant and ΔE is the energy gap tail interpreted as the width of the tail of localized states in the forbidden band gap. The Urbach formula was used to calculate the width of the Urbach tail of the localized states due to the defect levels in the transition gap.

The complex refractive index is given by:

$$n^* = n - ik \quad (4)$$

Where, k is the extinction coefficient and n is the refractive index and they can be calculated from the following equations^{16,17}:

$$k = \frac{\alpha \lambda}{4\pi} \quad (5)$$

$$n = \left\{ \left[\frac{4R}{(R-1)^2} - k^2 \right]^{1/2} - \frac{R+1}{R-1} \right\} \quad (6)$$

Where, R is the reflectance which determined from the absorption and transmittance spectra data.

On the other hand, if the refractive index and extinction coefficient are known, the real and imaginary parts of the complex dielectric constant of the nanocomposite can be also estimated. The real ϵ' and imaginary ϵ'' parts of the complex dielectric constant are expressed as¹⁸:

$$\epsilon' = n^2 - k^2 \quad (7)$$

$$\epsilon'' = 2nk \quad (8)$$

The refractive index is expressed by a single effective oscillator dispersion equation of the form¹⁹:

$$(n^2 - 1)^{-1} = \frac{E_0}{E_d} - \frac{1}{E_0 E_d} (\hbar \omega)^2 \quad (9)$$

Where, $\hbar \omega$ is the incident photon energy, E_0 is the single-oscillator energy for electronic transitions, and E_d is the dispersion energy.

3. Results and Discussion

The absorption coefficient $\alpha(\omega)$ values are calculated from the absorbance by using equation (1). Figure 1 shows the absorption coefficient of PVA: CuCl_2 films with different concentrations of CuCl_2 salts as a function of the wavelength. It can be seen the absorption is smallest at high wavelength. This means that the possibility of an electron transition is low because the energy of the incident photon is not sufficient to move the electron from the highest unoccupied molecular orbital to the lowest occupied molecular orbital²⁰. The increase

in absorbance with the increase in weight percentage of the added CuCl₂ can be explained by the fact that copper chloride ions absorbed the incident light fall on them. In other words, ions absorb the incident light by the free electrons.

From the linear part of the plots of $(\alpha h\nu)^2$ against $(h\nu)$ for the PVA:CuCl₂ films as shown in Figure 2, the optical energy gap values have been determined according to equation (2). As illustrated in Figure 2, the intercept of the extrapolation of the linear portion of these curves to zero absorption on $h\nu$ axis, gives the value of optical band gap energy E_{opt} .

The determined values of optical band gap energy for all samples are presented in Table 1. From Table 1, the values of E_{opt} reduced significantly from 3.24 eV for pure PVA to 2.94 eV for PVA complexed with 12 wt% CuCl₂. It was reported that the modification in electronic structure may affect the optical properties of SPEs²¹. The decrease in E_{opt} values is a consequence of the generation of new energy levels (traps) between the highest occupied molecular orbital and lowest unoccupied molecular orbital, due to the formation of the disorder in the SPEs films. This leads to an increased density of the localized states in the mobility band gap of the PVA matrix.

To realize the formation of defects in PVA host polymer, the width of the tail of localized states within the forbidden band gap energy was calculated from the exponential region of the UV-visible absorption spectra. At the lower absorption coefficient $\alpha(\omega)$ level, the values of $\alpha(\omega)$ are described by

the Urbach formula (equation 3). Figure 3 presents the plots of $\ln(\alpha)$ against photon energy $(h\nu)$ for pure and doped PVA films. The ΔE values are calculated from the reciprocal of the slope of the linear part of each curve, and they are inserted in Table 1. It is evident that the energy tails values increase from 0.67 eV for pure PVA to 0.91 eV for 12 wt% CuCl₂ composites. The smallest value of energy tails for PVA can be ascribed to the semi-crystalline nature of PVA.

Thus, the increase in ΔE for doped samples suggests the increase of the amorphous portion. The addition of salts to polymers may produce many trapped, which reduces the values of optical band gap energy of the SPE films²². The increase of energy tails ΔE as the concentration of CuCl₂ increases is consistent with the drastic decrease of the optical band gap energy E_{opt} . In general, the sum ($E_{opt} + \Delta E$) represents the mobility band gap energy; Table 1 contains values of the mobility gap for investigated SPE samples. The decrements in the mobility band gap energy values can be explicated by the fact that increasing in the CuCl₂ content could lead to the formation of ionic complexes, disorder, and imperfections in the structure of the host polymer, leading to create new localized states of various depths in the forbidden band gap energy. This usually contributes to the decrease in the optical band gap energy²³.

The extinction coefficient (k) is calculated using equation (5). The change of the extinction coefficient for the PVA:CuCl₂ films with different concentrations of CuCl₂

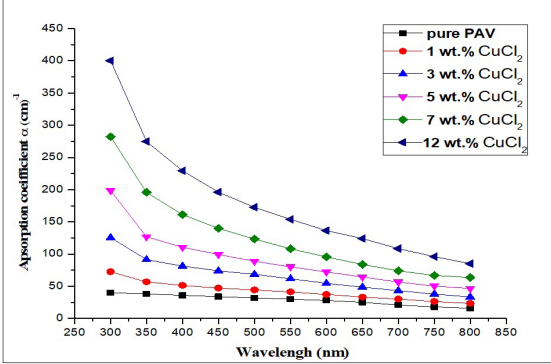


Figure 1. The absorption coefficient for PVA:CuCl₂ films as a function of the wavelength.

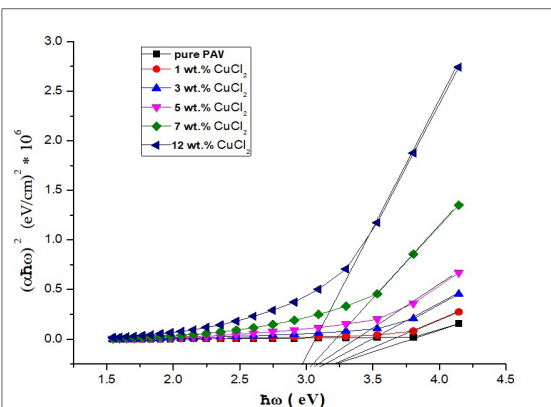


Figure 2. $(\alpha h\nu)^2$ versus photon energy $h\nu$ for PVA:CuCl₂ films.

Table 1. Optical energy results for PVA:CuCl₂ composite films.

CuCl ₂ wt%	Optical band gap E_{opt} (eV)	Energy gap tail ΔE (eV)	$E_{opt} + \Delta E$ (eV)
Pure PVA	3.25 ± 0.108	0.67 ± 0.0072	3.92 ± 0.1082
1	3.18 ± 0.091	0.72 ± 0.0074	3.90 ± 0.0913
3	3.12 ± 0.076	0.76 ± 0.0077	3.88 ± 0.0764
5	3.05 ± 0.066	0.81 ± 0.0080	3.86 ± 0.0665
7	3.00 ± 0.058	0.85 ± 0.0082	3.85 ± 0.0586
12	2.92 ± 0.052	0.91 ± 0.0085	3.83 ± 0.0527

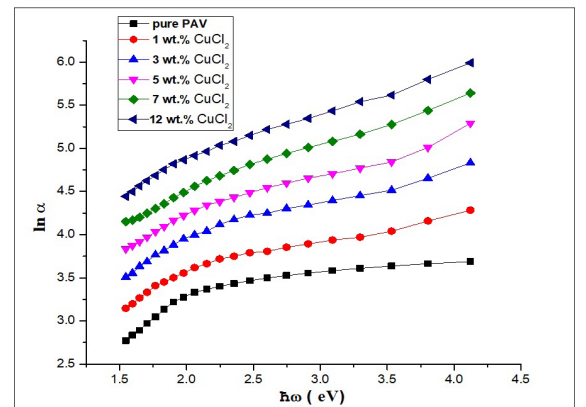


Figure 3. The plot of $\ln(\alpha)$ against photon energy $(h\nu)$ for PVA:CuCl₂ films.

salts as a function of the wavelength is shown in Figure 4. It can be noted that the extinction coefficient has lowering values at low concentrations, but it increases with increasing the weight percentage of the added CuCl_2 . This is attributed to an increased absorption coefficient with an increased percentage of added CuCl_2 .

The refractive index (n) is calculated from equation (6). Figure 5 shows the variation of refractive index for PVA: CuCl_2 films with different concentrations of CuCl_2 salts as a function of the wavelength. From the figure, we can see that the refractive index increases with increasing CuCl_2 concentrations. The reason for this result is an increase in the number of free electrons²⁴. The refractive index decreases with increasing wavelength, this behavior may be a result of the variation of the absorption coefficient which leads to spectral deviation in the location of the charge polarization at the attenuation coefficient due to the losses in the energy of the electron transition between the energy bands.

The real and imaginary parts of the dielectric constant (ϵ' , ϵ'') for PVA: CuCl_2 films with different concentrations of CuCl_2 have been calculated by using equations (7) and (8), respectively. Figure 6 and Figure 7 show the change of (ϵ') and (ϵ'') as a function of the wavelength. It can be seen that (ϵ') and (ϵ'') increase with increasing the concentration of added CuCl_2 , and this behavior is like (n) and (k) because (ϵ') depends on (n^2) due to low value of (k^2), while (ϵ'') is dependent on (k) value that change with the change of the absorption coefficient due to the relation between (α) and (k)²⁵.

The dispersion parameters E_o and E_d of the PVA: CuCl_2 films were evaluated by using equation (9) according to the Wemple DiDomenico model. E_d represents the dispersion energy associated with the average strength of the optical transitions and E_o simulates the excitation of electrons²⁶. The dispersion energy E_d , which is a measure of the inter-band optical transition intensity, is a significant factor in calculating the materials dispersion parameters^{27,28}. Plotting $(n^2-1)^{-1}$ versus $(\hbar\omega)^2$ for PVA: CuCl_2 films, we have got straight lines as shown in Figure 8. The values of E_o and E_d were calculated from the slope and the intercept (E_o/E_d) on the vertical axis, and then listed in Table 2 which shows that E_o and E_d values increased with the CuCl_2 concentration while the optical band gap values decreased.

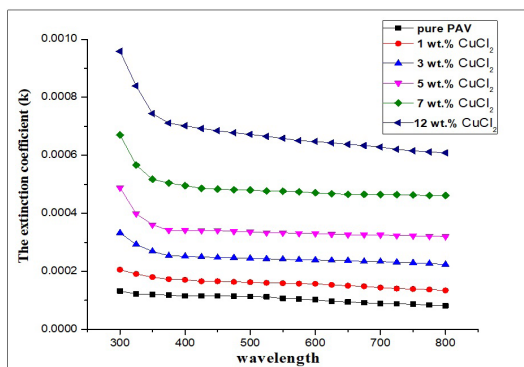


Figure 4. The Extinction coefficient for PVA: CuCl_2 films as a function of the wavelength.

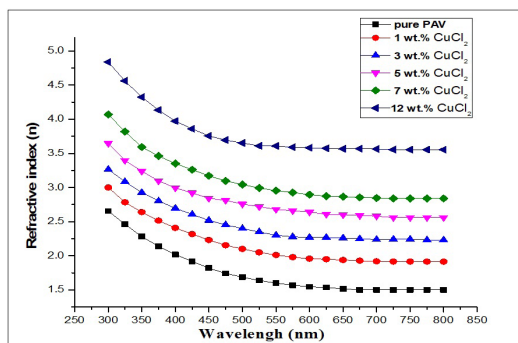


Figure 5. The variation of the refractive index (n) with UV wavelength.

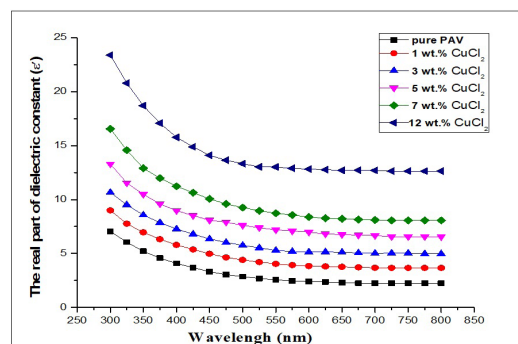


Figure 6. The real part of dielectric constant for PVA: CuCl_2 films as a function of the wavelength.

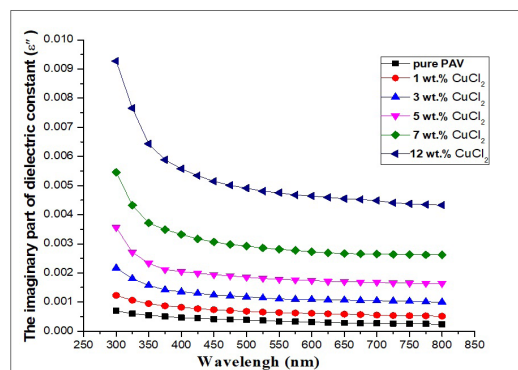


Figure 7. The imaginary part of dielectric constant for PVA: CuCl_2 films as a function of the wavelength.

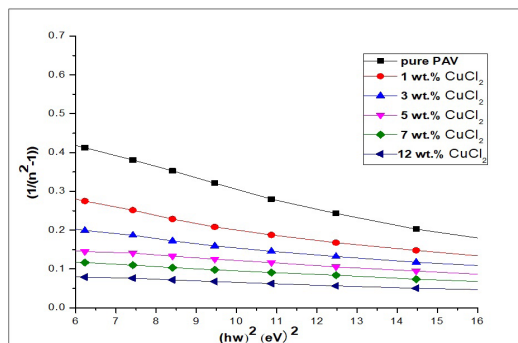


Figure 8. The variation of $(n^2-1)^{-1}$ with $(\hbar\omega)^2$.

Table 2. The dispersion parameters E_0 and E_d of the PVA:CuCl₂.

CuCl ₂ wt%	Single-oscillator energy parameter E_0 (eV)	Dispersion energy parameter E_d (eV)
Pure PVA	4.14	4.56
1	4.61	10.84
3	4.94	17.61
5	5.14	26.72
7	5.22	32.54
12	5.64	42.53

4. Conclusions

In this work, the effect of CuCl₂ impurity on the optical properties of PVA films has been studied using the solution cast technique. The absorbance and the absorption coefficient for PVA:CuCl₂ films increase with increasing the filler content (wt. %). The optical constants of polyvinyl alcohol (absorption coefficient, refractive index, extinction coefficient, real and imaginary dielectric constant) are increasing with the increase of concentrations of CuCl₂.

In general, the energy band gap of polyvinyl alcohol decreases with the increase of concentrations of CuCl₂, while the energy gap tail ΔE values increase.

The values of dispersion energy E_d and single-oscillator energy E_0 parameters according to the Wemple DiDomenico model were determined for the PVA:CuCl₂ thin films. These values increase with the increase of the CuCl₂ concentrations.

5. References

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