Fabrication and Study the Optical Properties and Dispersion Parameters of PVA/PAAm with CuNW Additive

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Abstract

Due to the scientific, industrial, electrical, and medical importance, it was necessary to study the properties of overlapping nanocomposites. Therefore it gained attention and directed scientists and researchers in the study of its structure and optical characteristics and other characteristics. In the present work, the influence of Copper Nanowire (CuNW) addition on several optical characteristics of polymers was investigated. For this purpose, many films have been made by adding CuNW to polymers with various weight percentages of (CuNW) with polymer utilizing the casting method. The structure of the nanocomposite (PVA-PAAm-CuNW) Optical microscopy was used to investigate the morphology of the samples, which revealed an excellent distribution of CuNW in the blend. Using a visible ultraviolet spectrophotometer to investigate the optical properties and record the absorption spectrum. The wavelength range of (190-1200) nm was used to record absorption spectra. The extinction coefficient, the CuNW addition increased the refractive index, while both the transmittance and the energy gap decreased. The Wemple–DiDomenico method was used to compute the dispersion parameters. E_d, E_o, n(0), M_{-1}, and M_{-3} decreased as the CuNW content in the PVA-PAAm-CuNW films increased. The obtained energy gap from this model agreed with the data obtained from Tauc model. These findings suggest that nanocomposites with such inclusions may be able to develop better and broader uses.

Key Words: PVA, PAAm, CuNW, Nanocomposites, Optical Microscopy, Dispersion Parameters.

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Introduction

In the recent years, polymer nanocomposites have become a prominent area of research (El-Bana *et al*, 2018; Al-Jamal *et al*, 2019; Al Asadi *et al*, 2019). They are involved in a variety of current industry and technological applications (Batte *et al,* 2018; Rezghi *et al*, 2019). This is due to their low cost, good flexibility, lightweight, easy processing, broadband and fast industrial processing (Hamdi *et al*, 2018; Cao *et al*, 2010; Khalid *et al*, 2020). Polymer optical characteristics are essential in the study of electronic transitions and the prospect of using them as optical filters, solar collector covers, selection surfaces, green houses, and medication delivery systems. (Pinto and Maaroufi, 2011; Khalid *et al*, 2021). The synthetic polymer poly (vinyl alcohol) (PVA) is an odorless, translucent, tasteless, or cream-colored granular powder that is odorless, translucent, and tasteless (Ravindra et al, 2015).

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PVA stands out from other polymers because of its strength, corrosion resistance, and high thermal stability. (Rajendran *et al*, 2004). PVA It is an industrial polymer that was used widely in the commercial, medical, industrial and food sectors in the first half of the twentieth century, and it was used in the manufacture of resins, lacquers, packaging materials, surgical threads, and other things (Demerlis and Schoneker, 2003; Tayser *et al*, 2015).

Many researchers were studied the improvement of optical, electrical, and mechanical properties of PVA polymer in blend with adding nanomaterial (Tuama *et al*, 2021; Al-Aaraji *et al*, 2019). Polyacrylamide (PAAm) is a water-soluble, swellable polymer with various application, including filtering aid and super absorbent. (Ahn and Castle, 2003). Polymers also exhibit novel and different characteristics when doped with noble metal nanoparticles. (Smith *et al*, 1997). Doping inorganic or organic nanoparticles into a polymer matrix can result in high-performance new materials that can be used in a variety of industries (Gautam and Ram, 2010). Transition metal oxides, such as copper, iron, nickel, cobalt, and zinc, have a variety of uses, including solar energy conversion, semiconductor, electronic, and electrical and optical switching devices. (Latifand and Abdullah, 2012). There's no denying that the Cu has attracted a lot of scientific and societal attention in recent decades. The Cu nanomaterials exhibited unique properties, containing thermal, optics, mechanics (Wang and Zhang, 2009). Cu NW films can achieve high optical transmittance with high electric conductivity (Cui *et al*, 2015; Han *et al*, 2014). Because the solution casting method is simple and cheap, it can be used to prepare polymeric blends or polymeric composites. (Sharba et al, 2020).

The aim of this study is investigating the effect of nano CuNW on the optical properties of a polymeric blend of PVA – PAAm.

Materials and Methods

The films of Polymer were produced by casting technique from mixing the PVA (purchased from Panreac / Spain, Lnc) With a molecular weight of (MW = 18000-12000) as well as purity (99.0%), PAAm (purchased from British Pharmaceutical Corporation (BDH) with a molecular weight that is 5000000 as well as purity (99.99%), and finally adding CuNW in varying proportions, supplier Houston USA, (Purity 99.5%, Diameter 100 nm, Length 10 μm) in 50 ml of distilled water. In a glass beaker equipped with a magnetic stirrer, the mixing process continued for 2 hours until a homogenous state is achieved of (PVA-PAAm) mixture was obtained at (70°C). Then the temperature (T°) of the PVA-PAAm matrix was reduced to about 40 ºC before adding the ratios of CuNW to prepare (PVA-PAAm-CuNW). Where the mixing of the PVA-PAAm-CuNW matrix was continued for another 1 h get fine homogenous and dispersion of CuNW in the polymers matrix. Then the mixture is left in the glass beaker for 24 hours. The solution was placed into a 5 cm diameter petri dish and allowed to dry for a week at room temperature. The samples' thickness was tested in micrometers and determined to be within (120) micrometers. The absorption spectra are recorded using ultraviolet irradiation in the range of 190-1200 nm.

Table 1. (PVA -PAAm- CuNW) Weight percentages

Sample	PVA (wt.%)	PAAm (wt.%)	CuNW(wt.%)
Sample 1	0.8	0.2	0.0
Sample 2	0.796	0.199	0.005
Sample 3	0.792	0.198	0.010
Sample 4	0.784	0.196	0.020

Results and Discussion

1. Optical Microscopy (OM)

Figure 1 shows optical images of PVA-PAAm and PVA-PAAm/CuNW samples with varied CuNW ratios at a magnification level of 100X. These photos demonstrate the matrices' excellent homogeneity, as well as a superior dispersion of CuNW during the polymer composites. The OM photos show that the PVA-PAAm/CuNW nano composites were successful preparation using the chosen process, with a noticeable alteration as the CuNW ratio increased. The contribution of these CuNW resulted in a number of alterations in the films without aggregation or a negative impact on the films' transparency. Increases in the ratio of CuNW increased the fine distribution as well., as illustrated in figure (1 D).

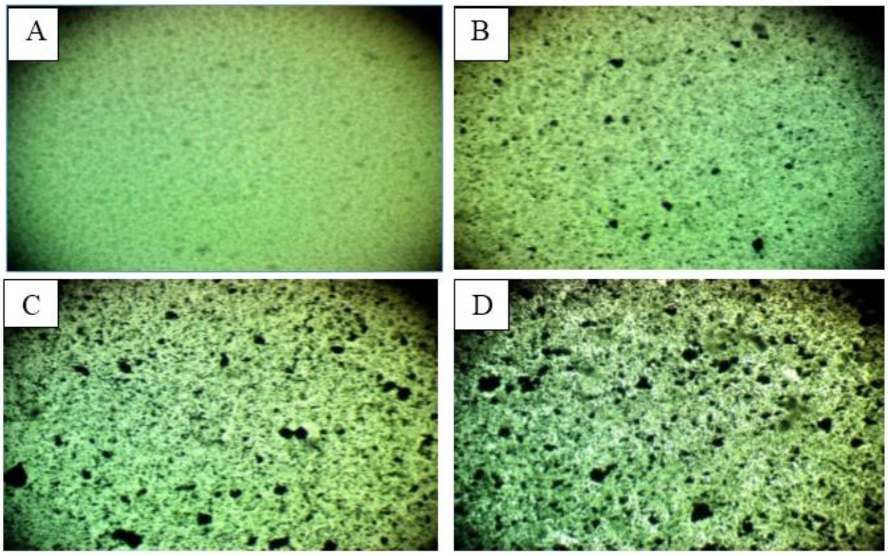

Figure 1. Photomicrographs (100X) of nanocomposites: A- (PVA-PAAm), B- (PVA-PAAm-0.005wt.%CuNW) and C- (PVA–PAAm-0.01wt.%CuNW) and C- (PVA–PAAm-0.02wt.%CuNW)

2. Optical Properties

Optical characteristics of PVA-PAAm films with varied CuNW ratios (0.5, 1, 2) wt.%. The film thickness was determined to be around 120 µm using a digital micrometer. Analyzing the absorption spectrum in the optical range (λ = 190 -1200) nm the assessment of optical properties of (PVA-PAAm-CuNW) films such as transmittance, absorption coefficient, extinction coefficient and refractive index, as well as energy gap.

Figure (2) shows the transmittance (T) as a function of wavelength (λ) of (PVA-PAAm-CuNW) nanocomposites with variou concentrations of CuNW, it can detect a decrease in transmittance. The additional CuNW include electrons that absorb electromagnetic energy and go to a higher energy level. Transmittance is high in the (pure) film. Because there are no free electrons, breaking the bonds demands a lot of energy. The transmittance (T) was calculated using the equation (Al-Huda *et al*, 2019):

$$T_r = \frac{I_T}{I_o} \qquad (1)$$

Where I_T means intensity of transmittance.

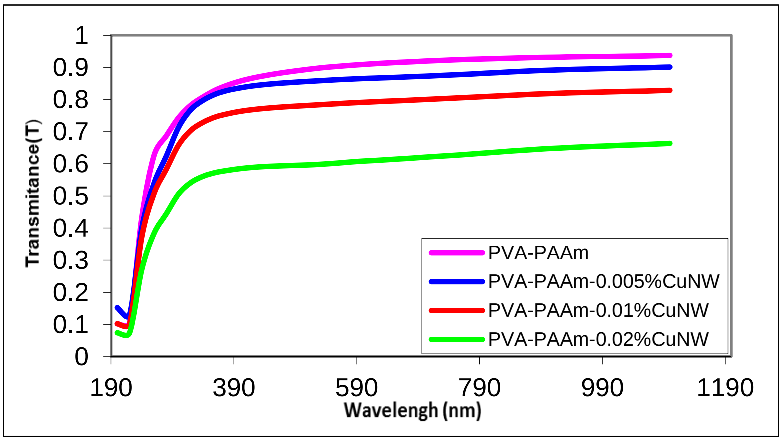

Figure 2. Transmittance of PVA-PAAm Blend vs. wavelength with various CuNW concentration

The absorption coefficient (α), which seen in Figure (3), decreased with increasing wavelength of the fabricated nanocomposites that depend directly with the absorbance (A) and film thickness (t). The α of PVA-PAAm-CuNW nanocomposites was calculated from the relation (Abass *et al*, 2018; Stenzel, 2005):

$$\alpha = \frac{2.303\ A}{t} \qquad (2)$$

The variation of the α with wavelength is presented in the Figure (3). It can be observe that the α was increased with increasing CuNW. Its values are less than (10^4 cm^{-1}) that give the indicating the indirect transitions (Khurana *et al*, 2016).

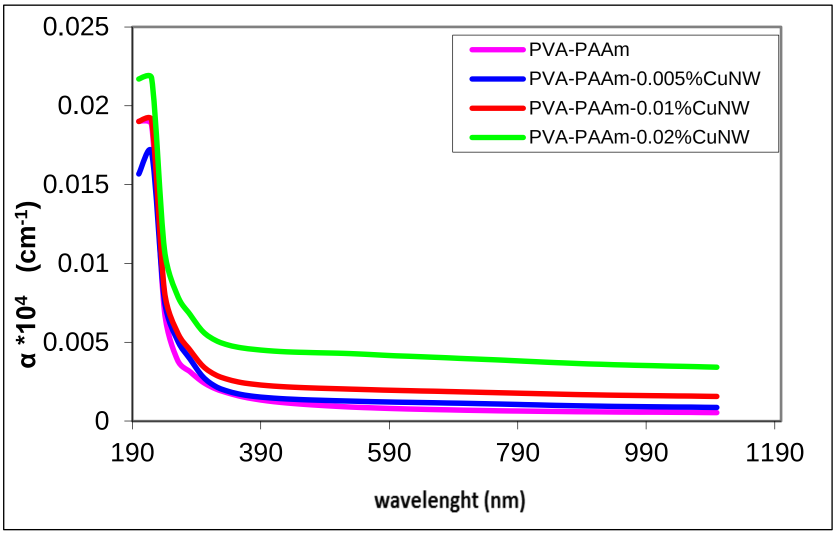

Figure 3. The absorption coefficient spectra of PVA-PAAm-CuNW Nanocomposites as a function of wavelength with various CuNW concentration

Extinction coefficient (k_o) was calculated by using equation 3. Figures 4 show how the extinction coefficient of PVA-PAAm-CuNW nanocomposites changes with wavelength. It must be observed that (k_o) has a low value at low concentrations, but it increases as the concentration of nanowires increases (CuNW). CuNW weight percentage increases have an effect, increasing the absorption coefficient (Suresh, 2013). a direct relation between the absorption coefficient and (k_o).

$$k_o = \frac{\alpha \lambda}{4\pi} \quad (3)$$

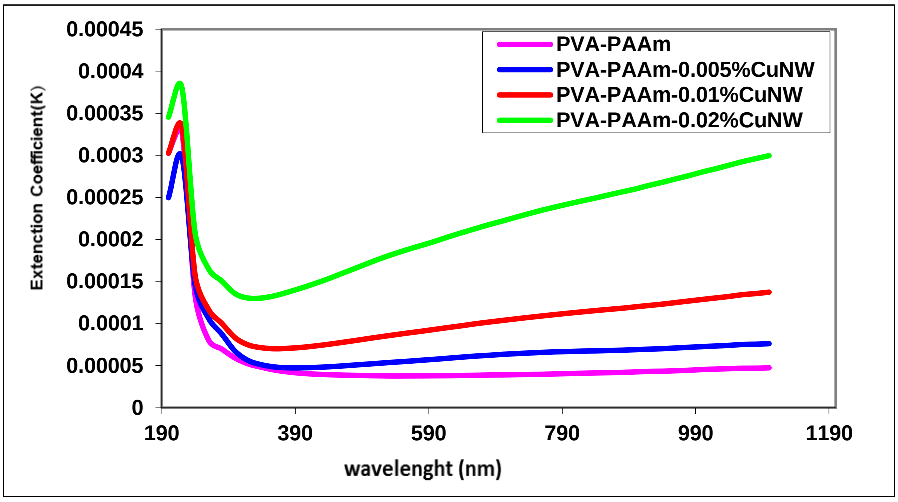

Figure 4. Extinction coefficient of PVA-PAAm-CuNW Nanocomposites as a function of wavelength with various CuNW concentration

The refractive index of (PVA–PAAm-CuNW) nano composites as a function of wavelength is shown in Figure 5. As seen in the picture, the refractive index of nanocomposites increases with increasing CuNW concentrations but decresed with increasing wavelength. This trend was linked to the density of nano composites increasing. When incident light interacts with a sample that has a high refractive index in the UV region, the refractive index values will increase. (Amin and Abd-El Salam, 2014; Khalid and Noor, 2019). The refractive index was calculated from the equation (4).

$$n = \sqrt{\frac{4R - k_0^{\,2}}{(R-1)^2}} - \frac{(R+1)}{(R-1)} \quad (4)$$

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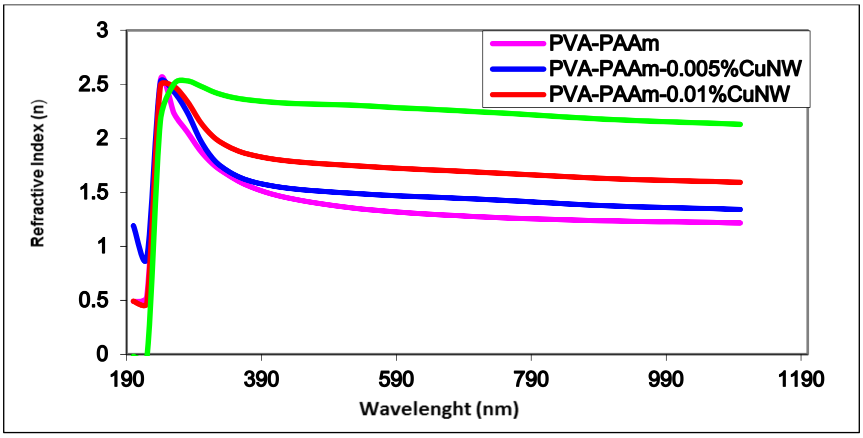

Figure 5. The refractive index (n) of PVA-PAAm-CuNW Nanocomposites as a function of wavelength with various CuNW contentration

"Optical Energy Gap" refers to the amount of energy needed to move electrons from low-energy states (valance bands) to higher-energy states (conduction bands) (Abass *et al*, 2018). The optical energy gap is a critical component for determining optical absorption. The material of the prepared film, the method of preparation, the doping process, the temperature of the doping process, the conditions of preparation, and the structure of the prepared films all have an impact (Khalid *et al*, 2016; Rasool *et al*, 2020). Figure 6 demonstrates the variation of energy band with photon energy. The magnitude PVA-PAAm-CuNW optical energy band gap (E_g) values were obtained by plotting photon energy $(\alpha h\upsilon)^{1/2}$ and absorption coefficient against photon energy (hυ) at room temperature, intersection of the linear portion of curve with axes was at point of $(\alpha h\upsilon)^{1/2} = 0$, which could be attributed to evidence of indirect electron transition. Tale 2 contains a list of energy gap vales. The decrease in the optical energy gap with increasing CuNW concentration could be due to structural deformation in the polymer films and an increase in the density of localized states in the band gap, causing the optical energy gap to shift to lower photon energy values. these findings are similar to those of a previous study involving the incorporation of CuNW into a polymer host material (Abass and Mohammed, 2019). The energy gap of the permissible indirect transition bands has been computed using equation (5) (Tauc *et al*, 1970; Alaa *et al*, 2020):

$$ah\upsilon = B(h\upsilon - Eg^{opt} \pm E_{ph})^{r} \qquad (5)$$

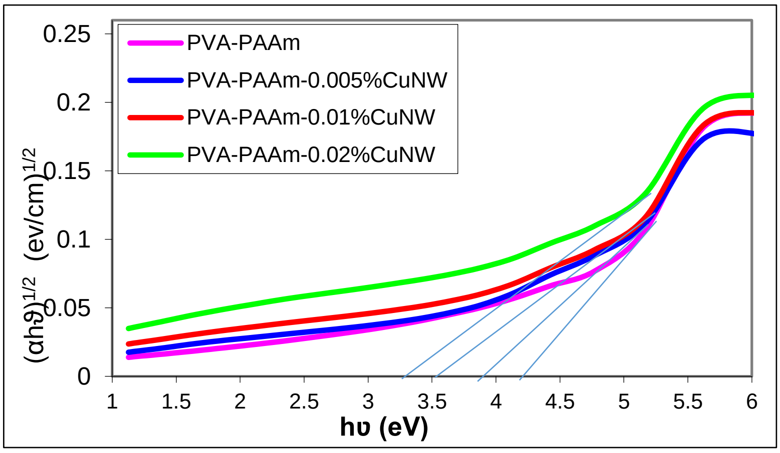

Figure 6. Plots of (hv)1/2 vs photon energy (h) of PVA-PAAm-CuNW Nanocomposites with various CuNW concentration

Table 2. Energy gap values at different CuNW

Sample	Eg(eV)
PVA-PAAm	4.20
PVA-PAAm-0.005%CuNW	3.80
PVAPAAm-0.01%CuNW	3.50
PVA-PAAm-0.02%CuNW	3.25

3. Dispersion Parameters

Dispersion parameters are critical in a variety of applications, including optical communication and optical device design. (Caglar *et al*, 2009). These parameters were introduced by

Wemple–Di Domenico according to the following equation (DiDomenico and Wemple, 1969):

$$(n^2-1)=\frac{E_d\,E_0}{{E_0}^2-(hv)^2} \qquad (6)$$

The refractive index is n, and the dispersion energy is E_d, while E_o is the single oscillator energy of the electronic transitions. A plot of $(n^2 - 1)^{-1}$ against $(hv)^2$, was used to estimate E_d and E_o which were calculated from the slope $(E_o\ E_d)^{-1}$ and intercept (E_o/E_d). The calculated values were listed in Table 3 that showing a decrease in their values with the increasing of CuNW concentrations. The value of the average energy gap can be calculated from the energy of the simple oscillator by the approximation relation ($E_o \approx 2E_g$). The value of the energy gap estimated by Wemple–DiDomenico was consistent with the value of the optical energy gap obtained from Tauc relation.

The static refractive index (n_o) and the static dielectric constant can be obtained from the following relations (Tigau, 2007; Ahmed *et al*, 2020):

$$n^2(0)=1+\frac{E_d}{E_0} \qquad (7)$$

$$\varepsilon_\infty = n^2(0) \qquad (8)$$

The calculated values were listed in the Table 3 showing a decrease in their values with the increasing of CuNW contents.

The M_{-1} and M_{-3} moments of the imaginary part of the optical spectrum of PVA-PAAm-CuNW films can be calculated using the following relationships. (Atyia, 2006):

$$E_0^2=\frac{M_{-1}}{M_{-3}} \qquad (9)$$

$$E_d^2=\frac{{M^3}_{-1}}{M_{-3}} \qquad (10)$$

According to Table3, optical spectrum M_{-1} and M_{-3} moments decrease when CuNW increases in the PVA-PAAm-CuNW system.

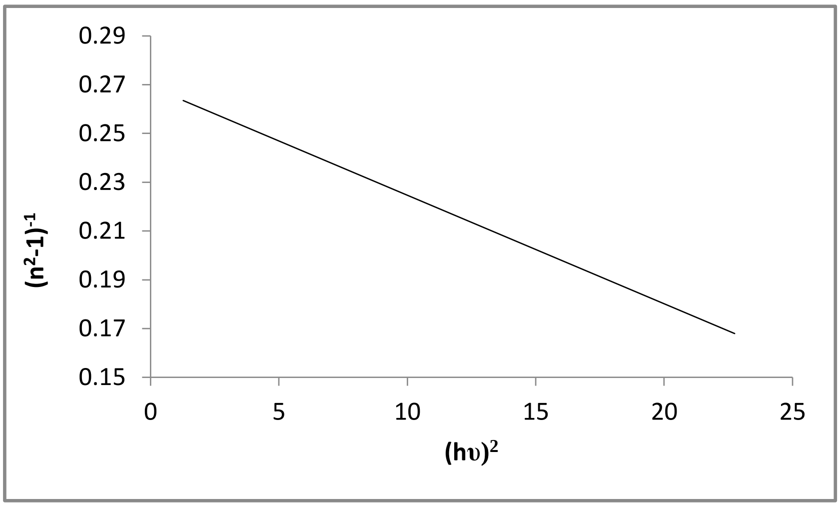

Figure 7. Plot of $(n^2 -1)^{-1}$ versus $(h\upsilon)^2$ of PVA-PAAm blend

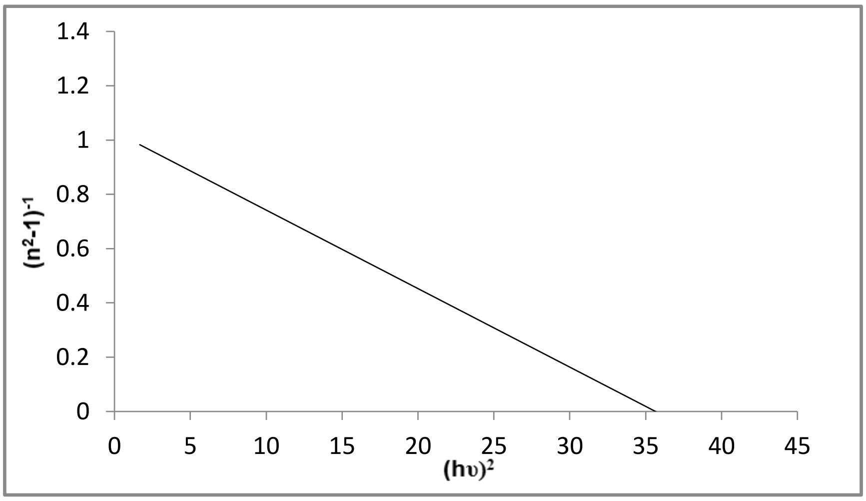

Figure 8. Plot of $(n2 -1)^{-1}$ vs $(h\upsilon)^2$ of PVA-PAAm-CuNw nano composite with 0.005% CuNW content

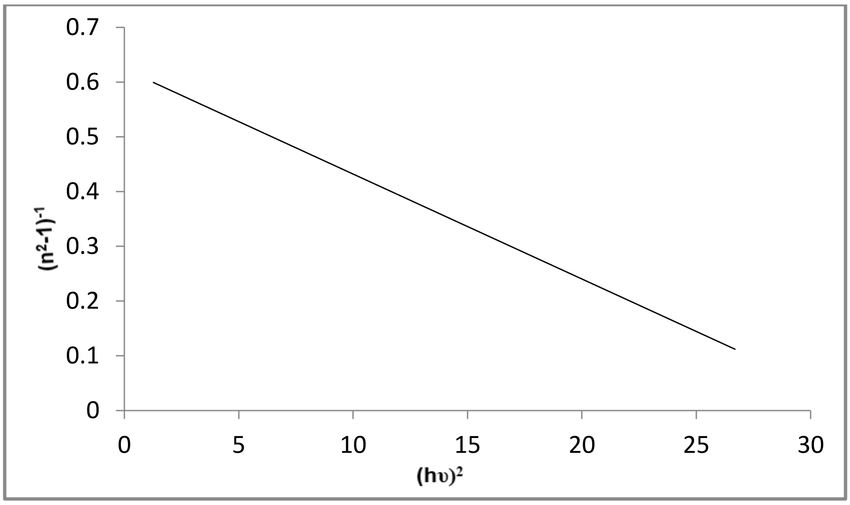

Figure 9. Plot of $(n^2 -1)^{-1}$ vs $(h\upsilon)^2$ of PVA-PAAm – CuNW nano composite with of 0.01% CuNW content

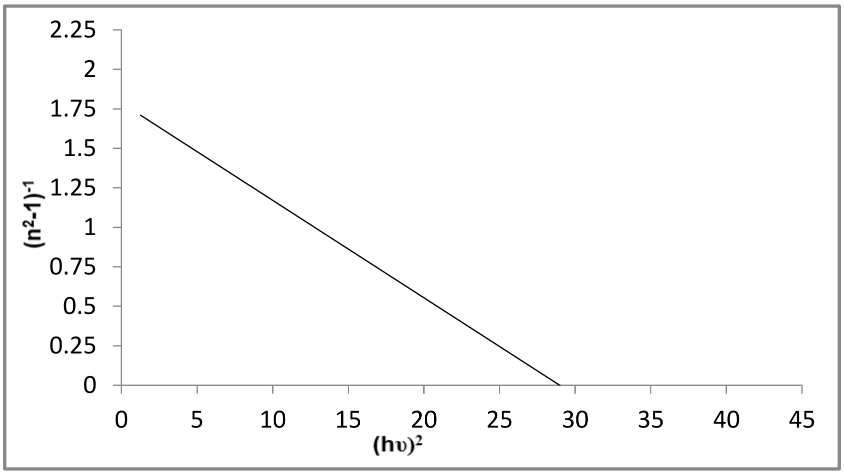

Figure 10. Plot of $(n^2 -1)^{-1}$ vs $(h\upsilon)^2$ of PVA-PAAm – CuNW nano composite with of 0.02% CuNW content

Table 3. Optical parameters of (PVA-PAAm-CuNW) nano composites

Parameter	PVA-PAAm			
	0.0	**0.005wt.% CuNW**	**0.01wt.% CuNW**	**0.02wt.% CuNW**
E_o	7.88	5.94	5.78	5.24
E_d	29.18	5.94	9.25	2.99
E_g	3.94	2.97	2.89	2.62
$n^2(0)$	4.70	2.00	2.60	1.57
$n_o(0)$	2.17	1.41	1.61	1.25
ε	4.70	2.00	2.60	1.57
M_{-1}	3.70	1.00	1.60	0.57
M_{-3}	0.06	0.03	0.04	0.02

Conclusion

PVA-PAAm-CuNW nanocomposite film with a thickness of 120m was successfully made using the casting method. Optical microscope pictures showed that the approach was successful in fabricating novel nanocomposites with uniform and fine dispersion, resulting in improved morphological qualities. Studying optical properties, CuNW contribution resulted in a significant improvement in optical characteristics. Absorption coefficient, extinction coefficient, refractive index, of the nanocomposites were increased by increasing concentrations of CuNW, while transmittance and the energy gap was decreased. Wemple–DiDomenico model was applied to these films in order to calculate the dispersion parameters and was found that all the parameters were decreased with CuNW content. The obtained energy gap from this model agreed with the data obtained from Tauc model.

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