JCBPS; Section C; August 2016 – October 2016, Vol. 6, No. 4; 1270-1280, E- ISSN: 2249 –1929

Journal of Chemical, Biological and Physical Sciences

An International Peer Review E-3 Journal of Sciences

*Available online at*www.jcbsc.org

Section C: Physical Sciences

CODEN (USA): JCBPAT Research Article

Preparation and Study of Some Optical Properties of ($PVA-FeCl_3$) Composites Films

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Received: 15 August 2016; **Revised:** 1 September 2016**; Accepted:** 13 September 2016

Abstract: The pure films of polymer (polyvinyl alcohol (PVA)) and doped then with iron chloride $FeCl_3$ salt with different concentrations ((1, 3, 5, 7 and 9) wt. %) have been prepared by using casting technique. The optical properties of pure and doped films were studied. The transmission and absorption spectra have been recorded in the wavelength range (250-1100) nm. The experimental results of ($PVA-FeCl_3$) composite film show that the transmittance decreases with increasing the filler content while the absorbance increases with increasing the filler content. The absorption coefficient, refractive index, extinction coefficient and real and imaginary parts of dielectric constant were found to increase with increasing the filler content. Moreover, the results show that the electronic transitions are allowed indirect transitions, the energy gap (Eg) and Urbach energy (Eu) decreases with increasing the filler content

Keywords: Optical properties, polyvinyl alcohol (PVA), Iron Chloride, Composites.

1. INTRODUCTION

Polymers, as plastics and rubbers, pervade our lives and we come across them in many different forms. As such, their physical properties have great importance and an understanding of them is vital for their uses in technology and engineering[1]. Polymers possess material properties which are distinctly different from those exhibited by metals, ceramics and glasses. Metals on heating can be transformed from hard solids to low viscosity liquids over a relatively small temperature range. Ceramics exhibit a hardness that does not very significantly with temperature up to the melting point and have poor impact properties and low elasticity. In contrast, polymers can be hard at low temperatures, comparable to metals or glasses, but on heating can be transformed into a rubbery state and exhibit a high degree of elasticity. Increasing the temperature further in certain cases allows the polymer to be converted into a free flowing liquid. However, some polymers do not flow when heated and so cannot be reshaped[1].Polyvinyl alcohol (PVA) is a water-soluble synthetic polymer. Due to the characteristics of easy preparation, good biodegradability, excellent chemical resistance and good mechanical properties, (PVA) has been used on many biomaterial applications[2]. Doping of polymers attracted the scientific and technological researchers, because of their wide applications. The dopant in polymer can changes the molecular structure and hence the microstructure as well as macroscopic properties of the polymer [3].

2. MATERIALS AND METHODS

The materials used in this work were a powder of polymer (polyvinyl alcohol (PVA)) doped with iron chloride $FeCl_3$ salt with weight percentage (0, 1, 3, 5, 7 and 9) wt%. It was dissolved in (15 ml) of distilled water in glass beaker by using magnetic stirrer for about (45 minute) and placed in Petri dish (5 cm diameter) using casting technique to prepare the films. The thickness of the dried films is (45 μm) measured by digital micrometer. The transmission and absorption spectra of (PVA-$FeCl_3$) composites films have been recorded in the wavelength range (250-1100) nm by using the UV-Visible 1800 double beam spectrophotometer provided by Shimadzu, Japanese company.

3. RESULTS AND DISCUSSION

3.1. Transmission Spectrum: Figure (1) shows the transmission spectrum for (PVA-$FeCl_3$) composites films with different concentrations of $FeCl_3$ salt as a function of the wavelength. The figure shows that the transmittance increases with the increase in the wavelength for all the composites films and afterwards it nearly remains same at higher wavelength.

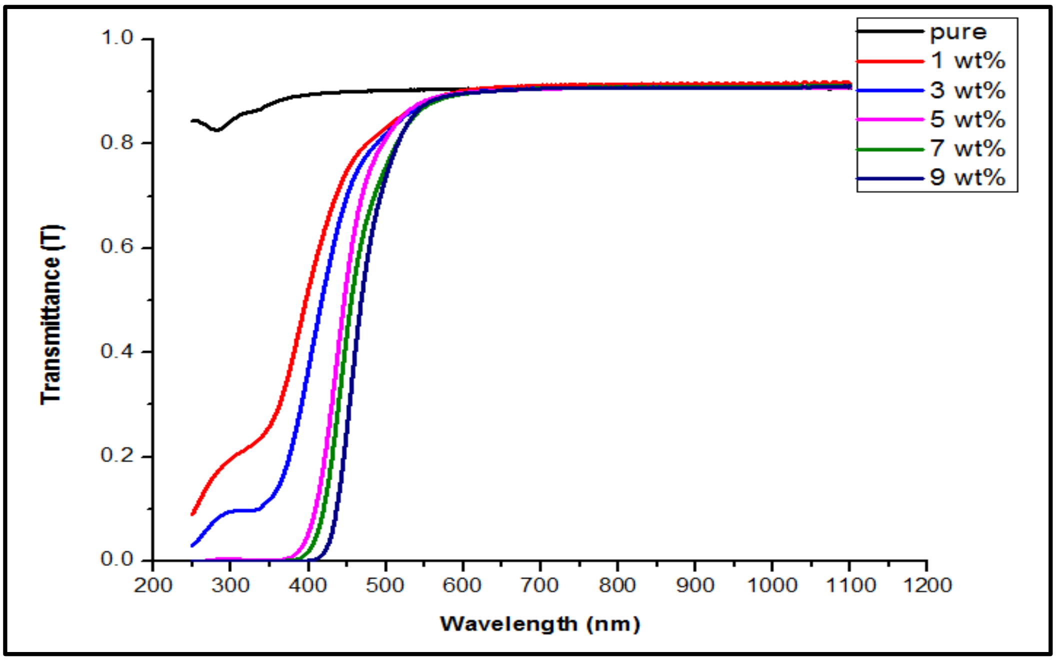


Fig.1: The transmittance for (PVA-$FeCl_3$) composite film with different concentrations of $FeCl_3$ salt as a function of the wavelength

And also the transmittance decreases with the increase in the weight percentage of the added $FeCl_3$ salt. This is caused by the added $FeCl_3$ salt which contains electrons in its outer orbits which can absorb the electromagnetic energy of the incident light and then the electrons travel to higher energy levels. This process is not accompanied by emission of radiation because the traveled electrons to higher levels have occupied vacant positions of energy bands, thus part of the incident light is absorbed by the substance and does not penetrate through it. On the other hand, the pure (PVA) film has high transmittance because there are no free electrons (i.e. electrons are linked to atoms by covalent bonds). This happens because the breaking of electron linkage and moving it to the conduction band need to photon with high energy [4].

3.2. Absorption Spectrum: Figure (2) shows the absorption spectrum for (PVA-$FeCl_3$) composites films with different concentrations of $FeCl_3$ salt as a function of the wavelength. It is shown that the adding of the filler $FeCl_3$ salt to the polymer (PVA) leads to increase the intensity of the absorbance peak. So, there is shifting in the position of the peaks for all amounts of filler adding to the polymer towards red wavelengths. The increase of absorbance with the increase in the weight percentage of the added $FeCl_3$ salt, can be explained by the fact that $FeCl_3$ salt ions absorbed the incident light on them [4-5].

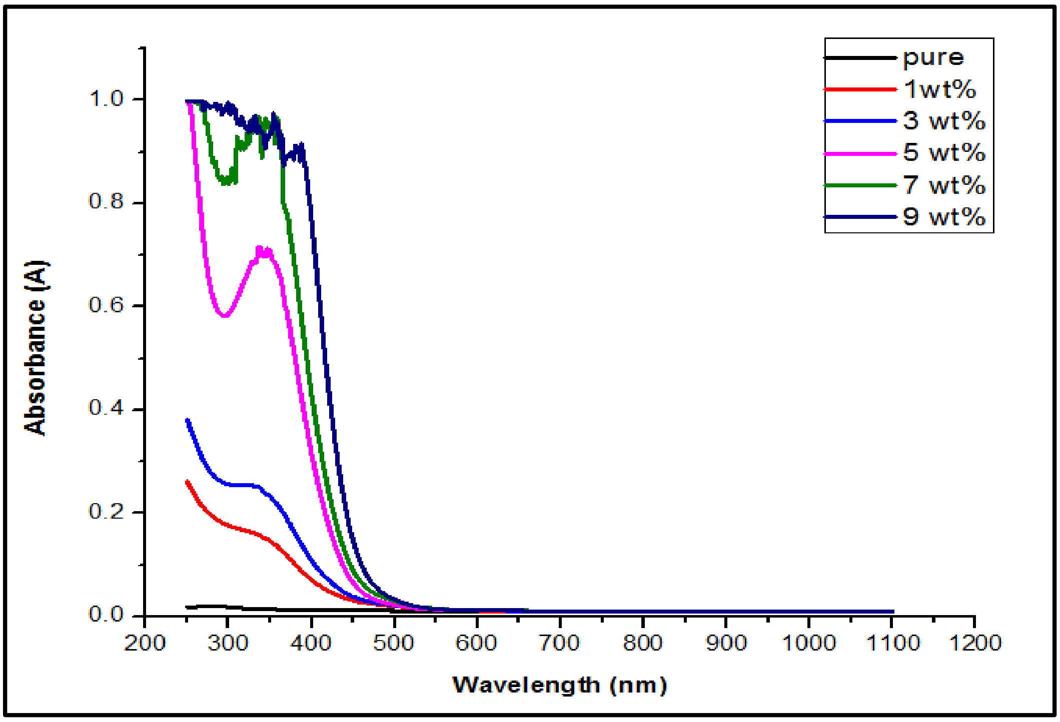


Fig.2: The absorbance for (PVA-$FeCl_3$) composite film with different concentrations of $FeCl_3$ salt as a function of the wavelength

3.3. Absorption Coefficient: Figure (3) shows the absorption coefficient for (PVA-$FeCl_3$) composites films with different concentrations of $FeCl_3$ salt as a function of the wavelength. The absorption coefficient α $(cm)^{-1}$ is calculated using equation [6]:

$$\alpha = 2.303\left(\frac{A}{t}\right)\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where (A) is the absorbance and (t) is the thickness of the film.

The figure shows that the absorption coefficient is high at high energies. This means that there is a high possibility for electron transition. Consequently, the energy of incident photon is enough to move the electron from the valence band to the conduction band, i.e. the energy of the incident photon is greater than the energy gap[4]. Also it is found that the absorption coefficient of ($PVA-FeCl_3$) composites films is less than (10^4 cm^{-1}), this explains that the electron transition is indirect. One can also see from the figure (3) that the absorption coefficient increases with increasing the weight percentage of the added $FeCl_3$ salt.

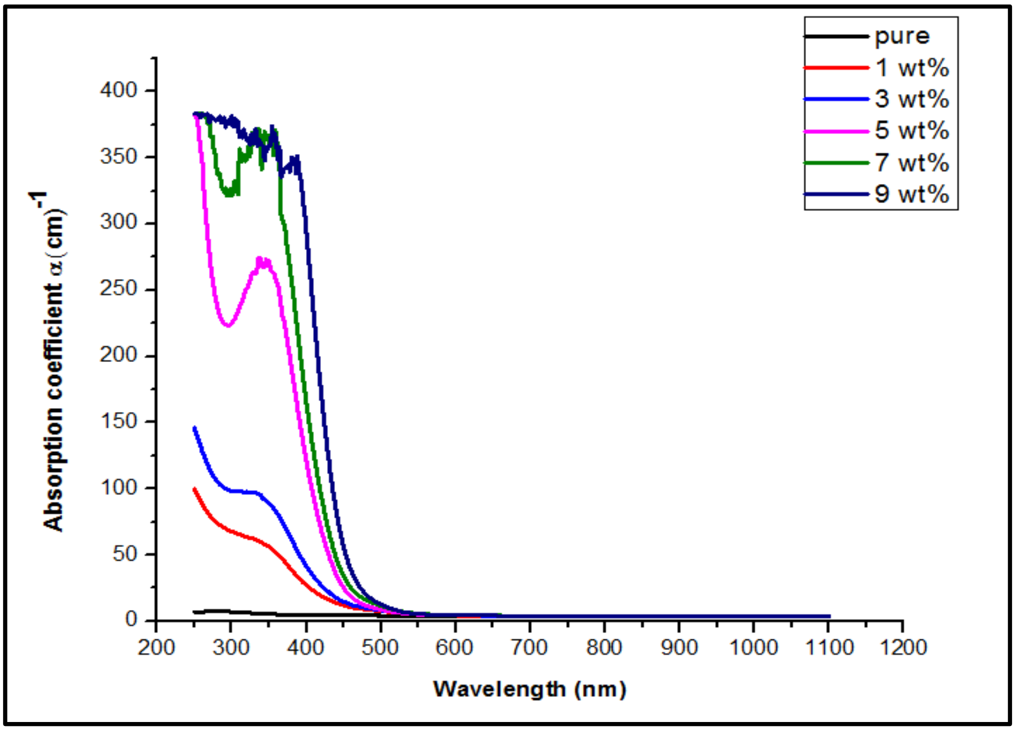


Fig.3: Absorption coefficient for ($PVA-FeCl_3$) composite film with different concentrations of $FeCl_3$ salt as a function of the wavelength

3.4. Energy Gap of The Allowed Indirect Transition: Figure (4) shows the relation between $(\alpha h\nu)^{1/2}$ vs. ($h\nu$) for ($PVA-FeCl_3$) composites films with different concentrations of $FeCl_3$ salt. The energy gap (E_g) for allowed indirect transition has been calculated by using equation[7]:

$$\alpha h\upsilon = B\left(h\upsilon - E_g\right)^2 \quad (2)$$

Where (B)is constant inversely proportional to amorphousity and (hυ) is the photon energy.

On drawing a straight line from the upper part of the curve toward the (x-axis) at the value $(\alpha h\nu)^{1/2}=0$ one get the energy gap (E_g) for the allowed indirect transition.The obtained values are shown in table 1.One can see that the values of energy gap (E_g) decreases with the increase in the weight percentage of the added $FeCl_3$ salt.

This is attributed to the creation of onsite levels in the energy gap (E_g), the transition in this case is conducted in two stages that involve the transition of electron from the valence band to the local levels and to the conduction band as a result of increasing the added weight percentage. This behavior is attributed to the fact that composites are of heterogeneous type (i.e. the electronic conduction depends on added impurities). The increase of the added rate provides electronic paths in the polymer which facilitate the crossing of electron from the valance band to the conduction band [4-8].

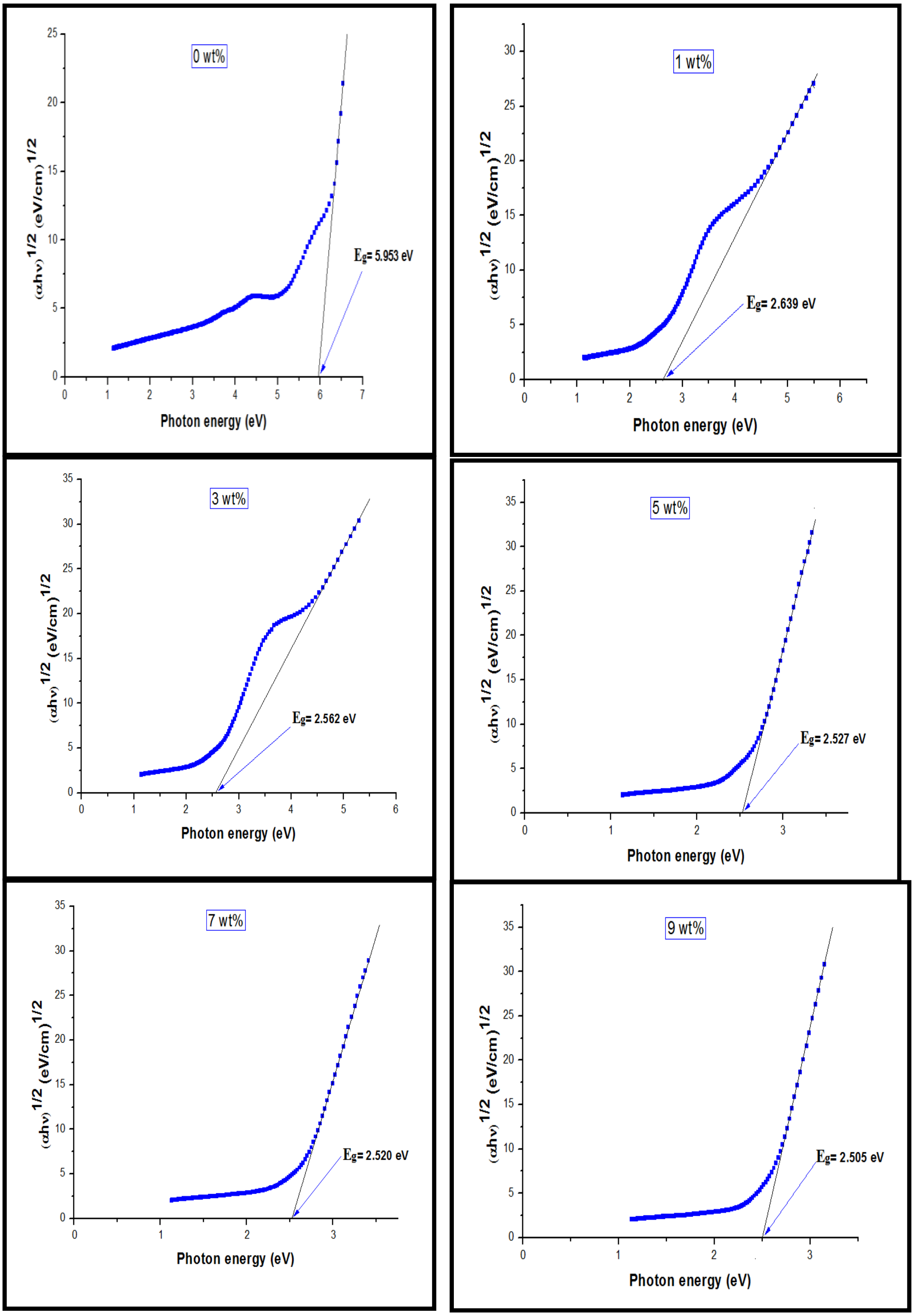


Fig.4: Energy gap (E_g) for the allowed indirect transition for (PVA-$FeCl_3$) composite film with different concentrations of $FeCl_3$ salt

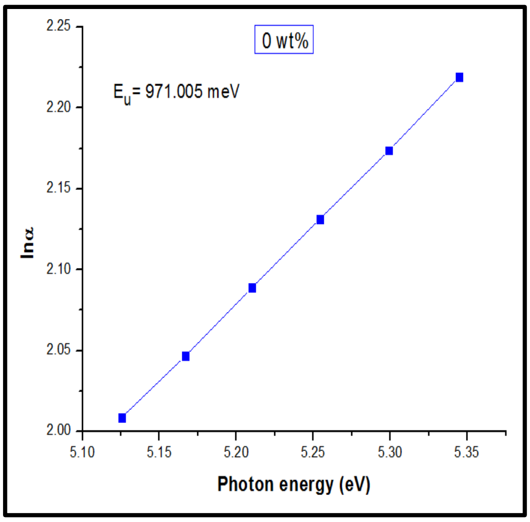
Table -1: Values of energy gap (E_g) for the allowed indirect transition for (PVA- $FeCl_3$) composite film with concentration of $FeCl_3$ salt

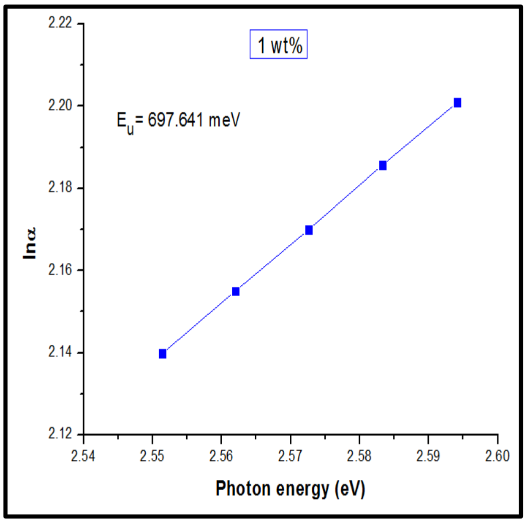
Concentration (Wt. %)	(PVA-$FeCl_3$) E_g (eV)
Pure (PVA)	5.953
1	2.639
3	2.562
5	2.527
7	2.520
9	2.505

3.5. Urbach Energy: The Urbach energy (E_u) has been calculated by using equation[9]:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right) \quad (3)$$

The Urbach energy for (PVA-$FeCl_3$) composites films with different concentrations of $FeCl_3$ salt were performed in figures (5). The values of Urbach energy was obtained from the inverse of the slope of (lnα) versus (hυ). The variation of the magnitude of Urbach energy in these composites films (decreases with increasing the weight percentage of the add $FeCl_3$ salt), which can be understood by considering the mobility concept as proposed by Davis and Mott, reveals that filling significantly affects the Urbach energy. The process of filling introduces additional defect states in the polymeric matrix. The density of localized states was found to be proportional to the concentration of these defects and consequently of $FeCl_3$ salt content. An increase in $FeCl_3$ salt content may cause the localized states of different colour centres to overlap and extend in the mobility gap. This overlap may give us an evidence of the considerable change in Urbach energy when $FeCl_3$ salt content is increased in the polymeric matrix. Table (2) shows the values of Urbach energy (E_u) for (PVA-$FeCl_3$) composites films with concentration of $FeCl_3$ salt.





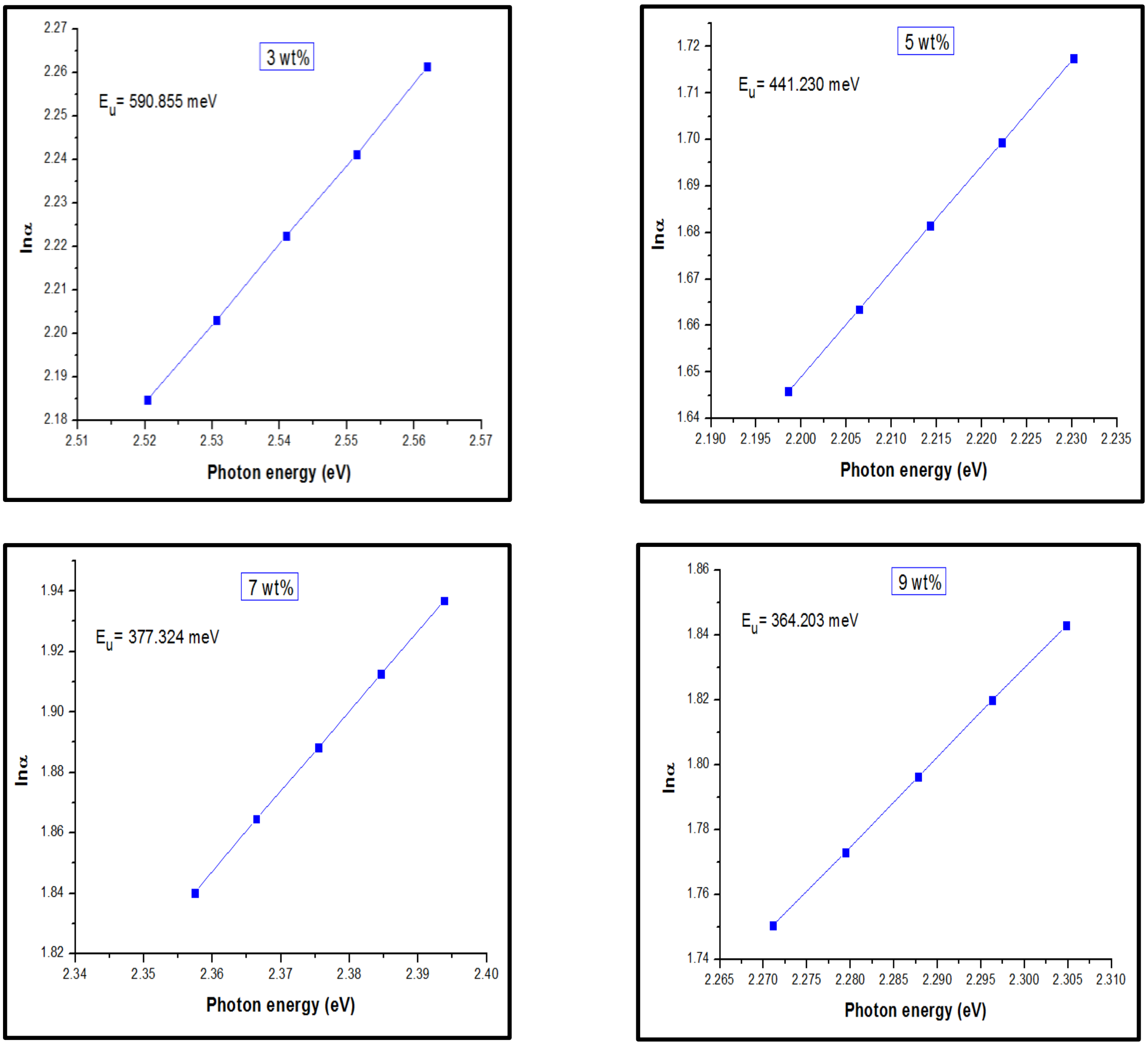


Fig.5: Urbach energy (E_u) for (PVA-$FeCl_3$) composite film with different concentrations of $FeCl_3$ salt

Table.2: Values of Urbach energy (E_u) for (PVA-$FeCl_3$ salt) composite film with concentration of $FeCl_3$ salt

concentration (wt %)	(PVA-$FeCl_3$) Eu (meV)
Pure (PVA)	971.005
1	697.641
3	590.855
5	441.230
7	377.324
9	364.203

3.6. Refractive Index: Figure (6) shows the variation of the refractive index for (PVA-$FeCl_3$) composites films with different concentrations of Fe Cl_3 salt as a function of the wavelength. The refractive index (n) is calculated from equation [10]:

$$n = \sqrt{\frac{4R - k_0^{\;2}}{(R-1)^2}} - \frac{(R+1)}{(R-1)} \quad \text{…………..……………………………} \qquad (4)$$

Where (R) is the reflectance and (k_o) is the extinction coefficient.

From the figure one can see that the refractive index increases with increasing the weight percentage of the added $FeCl_3$ salt.

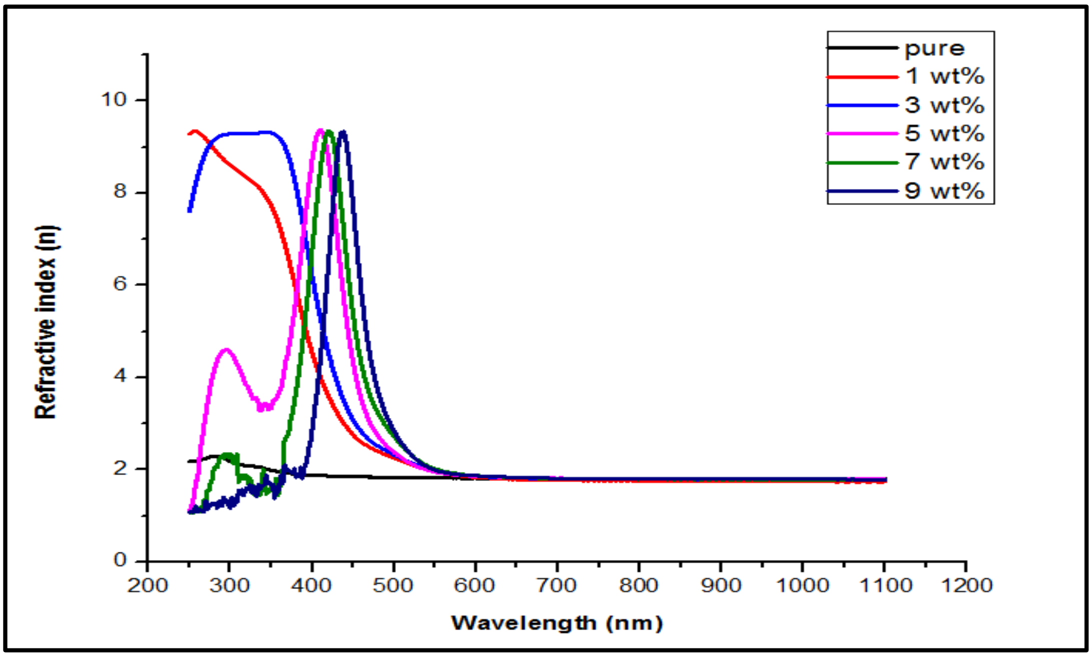


Fig.6: Refractive index for (PVA-$FeCl_3$) composite film with different concentrations of $FeCl_3$ salt as a function of the wavelength

3.7. Extinction Coefficient: Figure (7) shows the variation of the extinction coefficient for (PVA-$FeCl_3$) composites films with different concentrations of $FeCl_3$ salt as a function of the wavelength. The extinction coefficient (k_0) is calculated from equation [11]:

$$k_0 = {}^{\alpha\lambda}/_{4\pi} \quad \text{…………….……………………} \qquad (5)$$

Where (λ) is the wavelength of incident ray.

It can be noted that the extinction coefficient is of lowering values at low concentrations, but it increases with increasing the weight percentage of the added $FeCl_3$ salt. This is attributed to increased absorption coefficient with increased the weight percentage of added$FeCl_3$ salt.

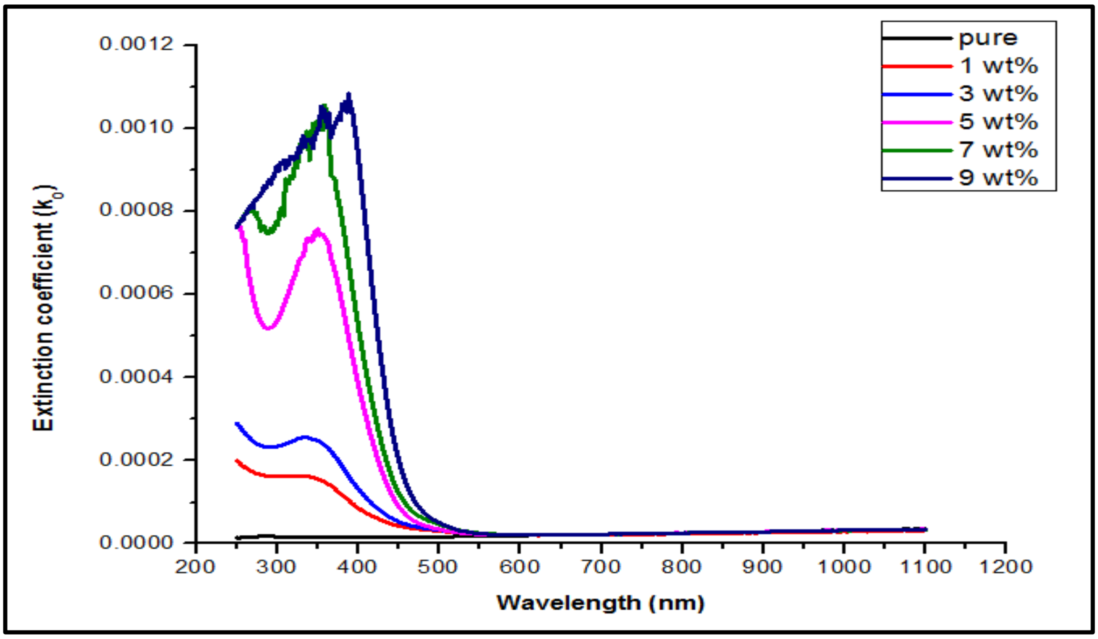


Fig.7: Extinction coefficient for (PVA-$FeCl_3$) composite film with different concentrations of $FeCl_3$ salt as a function of the wavelength

3.8. Real and Imaginary Parts of Dielectric Constant: Figures (8) and (9) show the vibration of the real and imaginary parts of dielectric constant for (PVA-$FeCl_3$) composites films with different concentrations of $FeCl_3$ salt as a function of the wavelength. The real (ε_1) and imaginary parts (ε_2) of dielectric constant can be expressed by the following equation [12]:

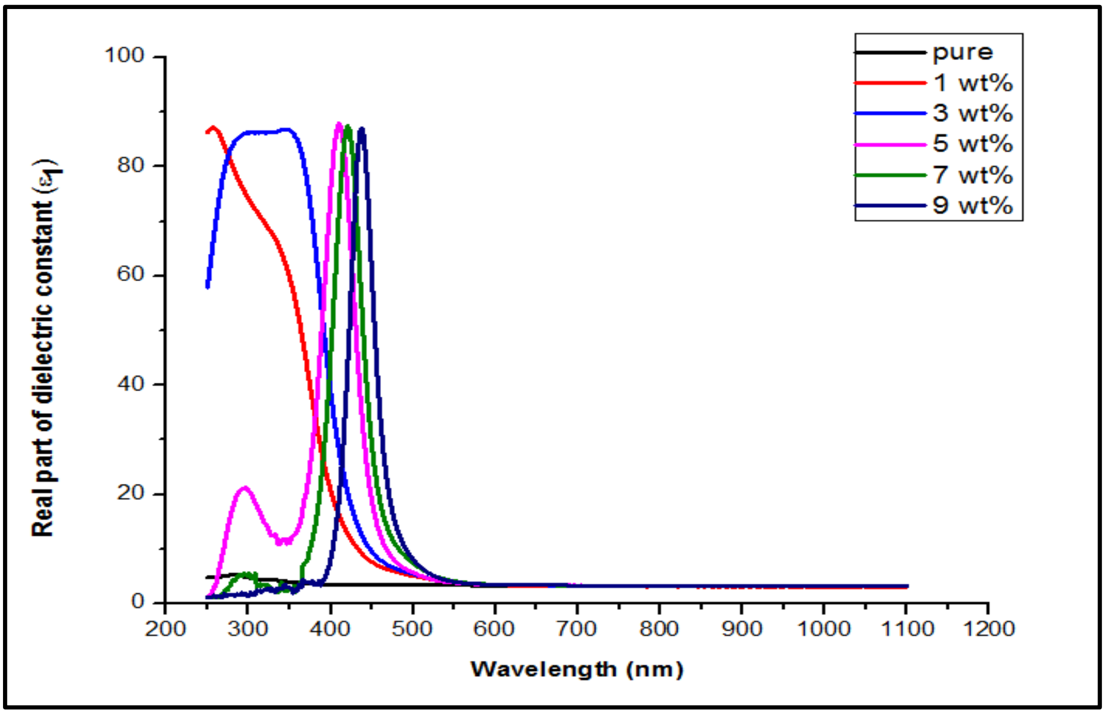


Fig.8: The real part of dielectric constant for (PVA-$FeCl_3$) composite film with different concentrations of $FeCl_3$ salt as a function of the wavelength

$$\varepsilon_1 = n^2 - {k_0}^2 \quad (6)$$

$$\varepsilon_2 = 2nk_0 \quad (7)$$

It can be seen that the real and imaginary parts of dielectric constant increases with increasing the weight percentage of the added $FeCl_3$ salt, and this behavior is similar to the behavior of (n) and (k_0) because (ε_1) depends on (n^2) due to low value of (${k_0}^2$), while (ε_2) is dependent on (k_0) that change (k_0) with the change of the (α) due to the relation between (α) and (k_0).

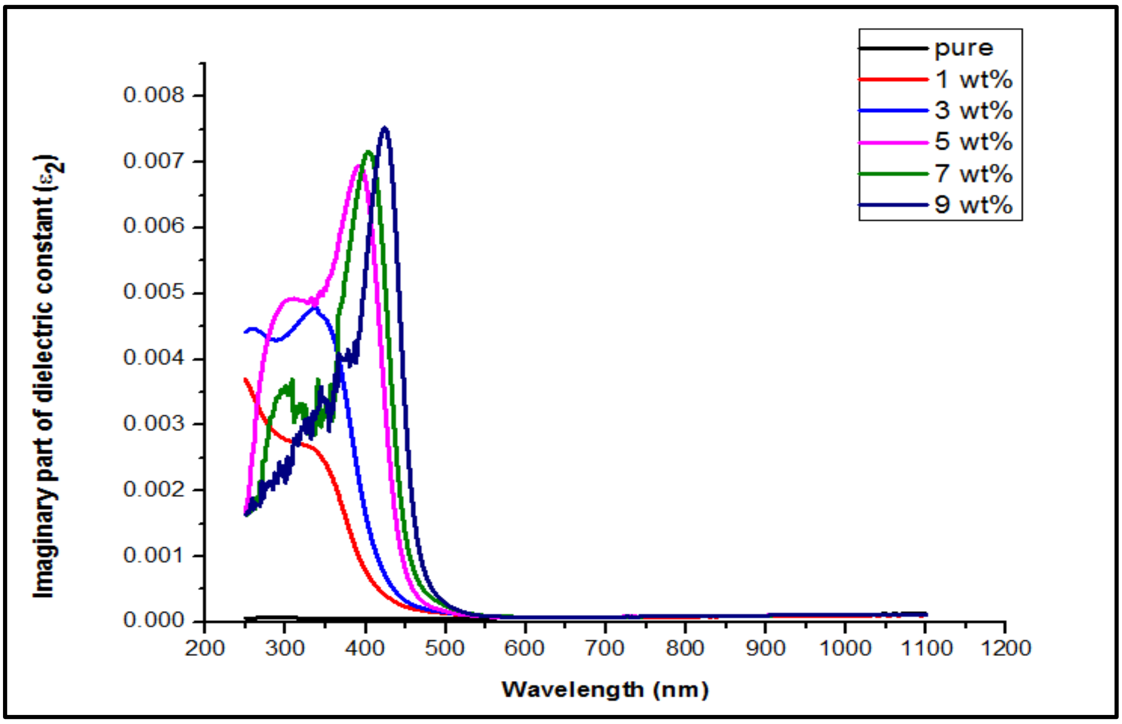


Fig.9: The imaginary part of dielectric constant for (PVA-$FeCl_3$) composite film with different concentrations of $FeCl_3$ salt as a function of the wavelength

4. CONCLUSIONS

1- The absorbance and the absorption coefficient of (PVA-$FeCl_3$) composite film increases with the increase in filler content (wt. %).

2- The absorption coefficient of (PVA-$FeCl_3$) composites films is less than ($10^4 cm^{-1}$); this means that the electronic transition is indirect.

3- Energy gap of allowed indirect transition and Urbach energy of (PVA-$FeCl_3$) composites films decreases with the increase in filler content (wt%), while refractive index, extinction coefficient and real and imaginary parts of dielectric constant increases with the increase in filler content (wt%).

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