Abstract - This paper investigates the effects of addition of Ag nanoparticles on optical properties of polyvinyl alcohol (PVA) and Polyethylene glycol (PEG-4000) blend. The samples of nanocomposites were prepared by adding Ag nanoparticles percentages of 0, 3, 6, 9 wt. % to the (PVA-PEG) blend. The films were prepared by casting method with different thicknesses. The absorption has been recorded in the wavelength range (200 - 1100) nm. The optical constants (absorption coefficient, extinction coefficient) energy gap of the indirect allowed and forbidden transition, real and imaginary dielectric constants have been determined. The optical constants are increase with increasing of silver nanoparticles concentration. The energy gap decreased with increasing the weight percentages of silver nanoparticle.

Keywords: Nanocomposites Films, PVA-PEG-Ag, Optical Properties.

1. INTRODUCTION

Over the past few years, a little word with big potential has been rapidly insinuating itself into the world's consciousness that word is "Nano" It has conjured up speculation about a seismic shift in almost every aspect of science and engineering with implications for ethics, economics, international relations, day-to-day life, and even humanity's conception of its place in the universe [1]. Nanotechnology or nanoscale science is concerned with the investigation of matter at the nanoscale, generally taken as the 1 to 100 nm range [2].

In nanotechnology, the primary role of classical physical principles is replaced as molecular and atomic dimensions are approached. Physical technical and chemical aspects influence the fabrication and the use and application of nanotechnological structures on an equal basis [3]. Composites can be defined as materials that consist of two or more chemically and physically different phases separated by a distinct interface [4]. In recent years, nanocomposites with practically all polymer systems have been used to improve one property or another, with varying degrees of success [5]. Polymers have drawn a considerable interest in device fabrication because of their extraordinary inherent properties like easy process ability, flexibility, high mechanical strength, etc. It is well documented electrical and optical properties of polymers can be improved to a desired limit through suitable doping [6,7]. Due to this exclusive combination, polymer–metal nanocomposites are considered as advantageous candidates [8], for device applications in various fields, like optics, mechanics, electronics, etc. Particularly, for opto-electronic and microelectronic devices, proper understanding of optical transitions and charge transport mechanism is very crucial [9]. Although, in the literature, there are reports indicating the optical behavior and electrical conduction mechanism in various doped polymers The selection of (PVA-PEG) as the base material is because of its good control on its conduction behavior after chemical and physical doping and providing a good host matrix for the embedding of metal nanoparticles [10,11]. The advantage of PVA and PEG that have the ability to blend into the water which is resistant to do solvents, oils, and have the ability exceptional adhesion materials cellulosic so use wide are used in making paper and textile industries in the manufacture of membranes resistance to oxygen in the coating photographic film [12]. Several authors have reported the improvement in the electrical, optical and dielectric behavior of (PVA-PEG) as an effect of adding various dopants like methyl orange, potassium thiocyanide, AgNO3, Cu, carbon black, Na, nano-Ag, etc. [13,14].

2. PREPARATION METHOD

Polymers nanocomposites films have been prepared by mixing (90%) of PVA with (10%) of PEG in (25) ml of distilled water, by using magnetic stirrer for the mixing process for 15 minutes to obtain more homogeneous solution with temperature (50 oC). Then adding the weight percentages of nano particle (3%, 6%, and 9%) of (Ag) and wait for 10 minutes to get mixture more homogenous, after that put the mixture in ultra-sonic bath for (5 minutes) in order to spread the nano particles and mixed fully with polymers blend and by using casting method we get the films from this mixture and casting each one of these ratios in the template (Petri dish) and then left for (3days) to dry mixture. Finally, the samples are ready to test the necessary measurements.

3. RESULTS AND DISCUSSION:

3.1 The absorbance of nanocomposites:
Absorbance can be defined as the ratio between absorbed light intensity (IA) by material and the incident intensity of light (Io) [15]
The absorbance of (PVA-PEG- Ag) nanocomposites with varies concentration over wavelength (200-1100) nm was recorded at room temperature. Fig (1) displays the variation of optical absorbance with wavelength for (PVA-PEG-Ag) nanocomposites. In these, Fig (1) note that the spectra reveal that all these films show more absorbance in ultraviolet region. All nanocomposites show that low absorbance in the visible region. This behavior can be explained as to interact with atoms, thus the photon will be transmitted. When the wavelength decreases (at the neighborhood of the fundamental absorption edge), the interaction between incident photon and material will occur, and the photon will absorbance [16], the intensity of the peak increasing and no shift in the peak position. The absorbance increases with increasing of weight percentages of the nanomaterials. This is due to absorb the incident light by free electrons [17].

\[ A = \frac{I}{I_0} \] ................................. (1)

3.2 Transmittance (T):

The transmittance (T) is calculated by using equation (2). Fig (2) shows the transmittance (T) as a function of wavelength for (PVA-PEG-Ag) nanocomposites,

\[ T = 10^{-A} \] ................................. (2)

where (T) is transmittance and (A) is absorption.

3.3 Absorption coefficient (a)

Absorption coefficient defined as a ratio decrement in flux of incident rays energy relative to the distance unit in the direction of incident wave diffusion.
\[ T = (1 - R)^2 \cdot e^{-\alpha t} \] 

where \( \alpha \) is the absorption coefficient, \( R \) is the reflectance and \( T \) is the transmittance.

The absorption coefficient \( \alpha \) (cm\(^{-1}\)) is calculated by using equation (3). Fig (3) shows the absorption coefficient \( \alpha \) (cm\(^{-1}\)) as a function of wavelength for (PVA-PEG-Ag) nanocomposites. It can be seen that the absorption coefficient is the smallest at high wavelength and low energy, this means that the possibility of electron transition is little because the energy of the incident photon is not sufficient to move the electron from the valence band to the conduction band \((h\nu < E_g)\) [18]. At high energies, absorption is bigger, this means that a great possibility for electron transitions consequently, the energy of incident photon is enough to move the electron from the valence band to the conduction band, the energy of the incident photon is greater than the forbidden energy gap. This shows that the absorption coefficient assists in figuring out the nature of electron transition, when the values of the absorption coefficient are high \((\alpha > 10^4)\) cm\(^{-1}\) at high energies it is expected that direct transition of electron occur, the energy and moment are maintained by the electrons and photons. But when the values of the absorption coefficient are low \((\alpha < 10^4)\) cm\(^{-1}\) at low energies, it is expected that indirect transition of electron occurs, and the electronic momentum is maintained with the assistance of the phonon [19], the results is that the coefficient of absorption for the (PVA-PEG-Ag) nanocomposites is less than \(10^4\) cm\(^{-1}\) at all concentrations.

3.4 Refractive index \((n)\) and reflectance \((R)\)

The refractive index can defined as a ratio between velocity of light in vacuum \((C)\), and velocity inside the material. The value of refractive index \((n)\) calculated by using equation (4) depending on the reflectance and extinction coefficient \((K_0)\) [20]. As in the following equation:

\[
R = \frac{(n - 1)^2 + K_0^2}{(n + 1)^2 + K_0^2} \] 

where \((K_0)\) is the Extinction Coefficient. Fig (4) shows reflectance \((R)\). The absorbance \((A)\) and transmittance \((T)\) can also calculate from the following equation:

\[ R + A + T = 1 \]
Refractive index can express by the following equation:

\[ n = \sqrt{\frac{4R - k_0^2}{(R - 1)^2}} \]

\[ = \frac{(R + 1)}{(R - 1)} \]

\[ \text{…………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………  (6)

see Fig (5) which refer to refractive index. By assuming thickness of films is \((dt)\) that decreases intensity of incident photon by \((dl)\) which direct proportion with both of intensity \((I)\) and thickness \((dt)\) where \((\alpha)\) is constant proportion \[ (7) \]

If intensity of incident ray \((I_0)\) which incident on a material of thickness \((t)\) and intensity of transmittance ray \((I_T)\) then integration procedure, will obtain \[ (20) \]

3.5 Extinction coefficient \((K_0)\)

Extinction coefficient \((k_0)\) is calculated by using equation (9). The change of the extinction coefficient as a function of the wavelength is shown in figures (6) for (PVA-PEG-Ag) nanocomposites. It can be noted that \((k_0)\) is low value at low concentration, but it increases with the increasing of the concentration of nanoparticles (Ag). This is attributed to increased absorption coefficient with the increase of weight percentages of (Ag) nanoparticles. Absorption coefficient has a direct relation with \((K_0)\) as in the equation (9) \[ (21) \]
\[ K_0 = \frac{\alpha \lambda}{4\pi} \]  \hspace{1cm} (9)

where \( \lambda \): The wavelength of incident photon rays.

Both the allowed and forbidden indirect transition band energy gap has been calculated by using equation (10). When the value of \( r = 2 \), the allowed indirect transition band energy gap is calculated, but when the value of \( r = 3 \), the forbidden indirect transition band energy gap is calculated. Fig (7) shows the relation between absorption edge \((\alpha h\nu)^{1/2}\) for (PVA-PEG-Ag) nanocomposites as a function of photon energy \( \nu \) respectively , on drawing straight line from the upper part of the curve toward the \((x)\) axis at the value \((\alpha h\nu)^{1/2} = 0 \) we get the energy gap for the allowed indirect transition [21]. In tables, we can see that the values of energy gap decrease with the increasing of the weight percentages of silver nanoparticles. This attributed to the creation of site levels in the forbidden energy gap, the transition in this case is conducted in two stages that involve the transition of electron from the valence band to the local levels to the conduction band because of increasing the silver nanoparticles weight percentage. This behavior is attributed to the fact that nanocomposites are of heterogeneous type (i.e. The electronic conduction depends on added concentration), the increase of the silver nanoparticles provides electronic paths in the polymer which facilitates the crossing of electron from the valence band to the conduction band, which explains the decrease of energy gap with the increase of the silver nanoparticles. These results are similar to the results reached by the researchers [22]. The forbidden transition of the indirect energy gap is calculated in the same way, that we obtain the allowed transition of the indirect energy gap for the (PVA-PEG-Ag) nanocomposites.

\[ \alpha h\nu = B(h\nu - E_g^{opt})^r \]  \hspace{1cm} (10)

where \( E_g^{opt} \) Energy gap between direct transitions, \( B \) constant depended on type of material \( r \) exponential constant, its value depended on type of transition, \( r = 1/2 \) for the allowed direct transition, \( r = 3/2 \) for the forbidden direct transition.
Figure (8): The energy gap for the forbidden indirect transition ($\alpha h\nu$)$^{1/3}$ as a function of photon energy of (PVA-PEG-Ag) nanocomposites.

Table (1): The values of energy gap for the allowed and forbidden indirect transition for (PVA-PEG-Ag) nanocomposites.

<table>
<thead>
<tr>
<th>Silver nanoparticles wt.%</th>
<th>E$_g$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Allowed</td>
</tr>
<tr>
<td>0</td>
<td>5.269</td>
</tr>
<tr>
<td>3</td>
<td>4.4904</td>
</tr>
<tr>
<td>6</td>
<td>3.643</td>
</tr>
<tr>
<td>9</td>
<td>3.364</td>
</tr>
</tbody>
</table>

5. CONCLUSION
1- The absorption, transmittance and absorption coefficient for all (PVA-PEG-Ag) films nanocomposites increases with increasing of Ag wt. % nanoparticles.
2- Reflectance, refractive index and Extincsion coefficient nanocomposites films increasing with increasing silver nano additive.
3- As we noted also the energy gap of indirect transitions (allowed and forbidden) decreasing with increasing of Ag wt.% nanoparticles.

6. REFERENCES


