Zinc Oxide and Silver Nanoparticles Adding for Development of Morphological and Optical Properties of Poly(vinyl alcohol)/Poly(vinyl pyrrolidone) Blend Nanocomposites Films

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Abstract: Polymer blend (PVA-PVP) with ZnO and different wt.% of Ag NPs as a nanocomposites (NCs) films synthesized using solution cast method. The obtained products were successfully characterized using Fourier transform infrared (FT-IR), and optical microscopy (OM). Optical characterized were studied by UV-visible spectroscopy. FT-IR spectra confirmed the production of functional groups present in the polymer nanocomposite systems. The optimal value of transmittance for polymer blend film is about 98% in the regions Vis and NIR. Reduced the transmittance of the nanocomposites films towards ultraviolet rays qualifies it to use as a packaging for storage drugs. The indirect allowed and forbidden transition energy gaps values decreased with increasing the Ag NPs content . All other parameters under search were also affected by the level of additives.

Key words: PVA-PVP , ZnO & Ag NPs, Nanocomposites films , Optical properties.

1. Introduction:

In recent years, there were a lot of focus on the creation and research of diverse polymer blends as a way to improve a material's performance. Polymer mixes will have characteristics that differ from the individual polymers. It is determined by the miscibility of the parent polymers. The polymer blends are exciting because their characteristics may be adjusted by adding different salts and nanoparticles [1, 2, 3] .

PVA (Poly(vinyl alcohol)) is a promising polymer because of its unique properties, such as environmental friendliness, toxicity is non-existent, good water solubility, good electro-optical feacher, chemical stability, and good dielectric strength. The hydroxyl group in PVA can help generate an interpenetrating connection in a polymer composite by hydrogen bonding [4,5]. PVA has an ability to blend into the water and is resistant to do solvents, and oils . As a result, it's frequently employed in the paper and textile industries to make oxygen-resistant membranes , where the mp = 230 ºC for fully hydrolyzed grades ,180-190 ºC for partially hydrolyzed grades, and the glass transition is (75-85) ºC [6].

PVP (poly(vinyl pyrrolidone)) is a good water solubility, biodegradable polymer with fantastic features such as toxicity is almost non-existent, high dielectric constant, and compatibility. The connection between Polyvinyl alcohol (PVA) and Polyvinyl pyrrolidone (PVP) arises due to hydrogen bonding between the PVA hydroxyl group and PVP carbonyl group of [7,8]. Blends of PVA-PVP are used for wound dressing , replacement of articular cartilage, and as membranes for high energy electrochemical devices[9]. Polymer nanocomposites (PNCs) have become a popular research topic in recent years[10]. Because of their distinct physiochemical characteristics , silver (Ag) NPs are regarded an appealing catalyst material [11,12]. Metal oxide ZnO NPs is an n-type semiconductor with a 3.37 eV energy gap. This has opened up new possibilities in a variety of fields, including light emitting diodes, piezoelectric transducers, and photocatalysts [13,14,15].The current work deals with the synthesis of nanocomposites (PVA-PVP: ZnO and Ag) and the study of their structural and optical properties for antibacterial action.

2.Experimental part:

2.1. Materials

The polymers PVA (Molecular formula $(CH_2CH(OH))_n$, Mol. wt. = 160,000 g.mol^{-1}) and PVP (Molecular formula $(C_6H_9NO)_n$, Mol. wt. = 60,000 g.mol^{-1}) were imported from indi (Central Drug House, Ltd, Company). The additives nanomaterials were zinc oxide NPs ZnO (Mol. wt. = 81.408 g.mol^{-1}) is a white powder that is insoluble in water, and silver NPs Ag (20 nm - 30 nm) black powder that is poorly soluble in water and could be obtained from (SkySpring Nanomaterials, lnc ,2935 Westhollow Dr. Houston, TX 77082, Fax:281-870-8002).

2.2. Purification of PVA-PVP and its NCs

Films of nanocomposites blend (PVA-PVP) with ZnO and different wt.% of Ag NPs have been prepared by a simple solution casting method. It is expected that the strong hydrogen bond forming capacity of PVA will interact with PVP and thus offers a new polymer designated as (PVA- PVP) with improved properties such as the control of PVA porosity and super-molecular structure[16]. 0.8g

of PVA was dissolving in 60 ml of deionized water. The solution were prepared by mixing with a magnetic stirrer for 1hr at room temperature, then continue for another hour under ~80°C to get a good mix, afterwards, it was added 0.2g of PVP and Stir enough to get a homogeneous solution, then the solution casted into Petri dishe and solvent is allowed to vaporize slowly at room temperature conditions for 144 h. The synthesized dried film is take off from the Petri dishes and kept in vacuum desiccators. NCs films from PVA- PVP/ 5wt.% ZnO and different (1, 2, 3 and 4 wt.%) of Ag, was obtained according to the following: firstly used the solid state method for mixing the ZnO and Ag NPs alone, which include dissolving it by ethanol solvent with continuous grinding in a crucible ceramic for 90 min, then dried at 60°C for 4 hr before adding it to the polymer solution. Mixture of the polymers were continuing as in previous steps interspersed with the use of ultrasonic for an 15 mints to prevent any agglomeration even get a homogeneous solution. The casting film kept at RT conditions for 144 h to dry. The uniform thickness was (120±5) μm measured by Digital Vernier Caliper.

2.3 Descriptions

Fourier transform infrared FT-IR spectra (Bruker company, type vertex -70, German origin) were performed to investigate functional groups in polymer blend and its NCs with ZnO and Ag , between 500–4000 cm⁻¹. The UV-Visible spectrophotometer (Shimadzu UV-1650 PC, Phillips / Japanese company), used in the wavelength range (190 -1100) nm at RT to record the spectrum of transmission and absorption.

4. Results and discussion

4.1 Fourier transform infrared (FT-IR)

Figure (1) illustrates the FTIR spectra of PVA-PVP blend and its NCs with ZnO and different wt.% of Ag NPs . FTIR spectrum of pure blend is corresponding to the broadness stretching vibrations of O–H (PVA and PVP), medial alkyne (disubstituted) C≡C group, C=O stretching of the ester group carbonyl groups (PVA) , C=N stretching vibration occurs at 3274.36 cm^{-1} , 2360.45 cm^{-1} , 1653.12 cm^{-1} and 1243.13 cm^{-1} respectively[17]. The absorption peak at 1086.57 cm^{-1} corresponds to the C–O stretch for secondary alcohol were observed in PVP-PVA hydrogels. The IR spectra of (pure blend/ inorganic Nps) NCs contains all the characteristic peaks of PVA , PVP and the added Nps.

Comparing the characteristic wavenumbers of blend with those representing the NCs , it can be noticed that there are slightly shifted toward higher wavenumbers, as a result of the addition of different wt.% of Ag NPs especially at 3274.36 cm^{-1}. Also the transmittance decreases with the increasing ratios of Ag NPs that assigned to increase the density of NPs. From this analysis , it is understood that there are no new peaks of absorption , therefore no interactions between polymer matrix and NPs.
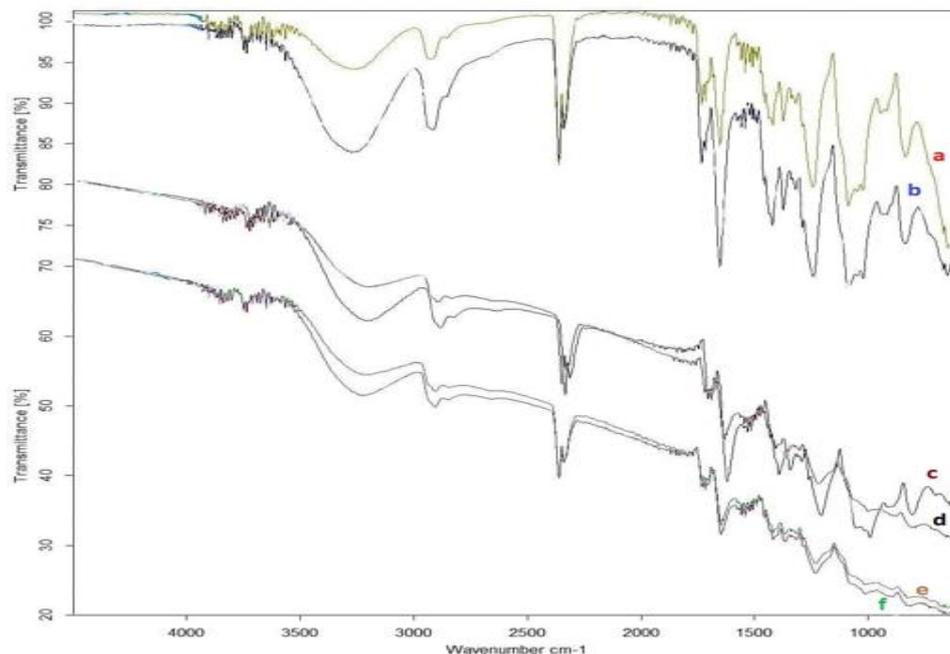
Fig.1: FTIR spectra of, a. (PVA-PVP) blend, b. (PVA-PVP/ 5wt.% ZnO), c. 1wt.% Ag, and d. 2wt.% Ag , e. 3wt.% Ag , f. 4wt.% Ag nanocomposite films .

4.2 Optical microscopy (OM) of the casting samples

The photomicrographs of the surface of (PVA-PVP) blend and it's nanocomposite with ZnO and different wt.% of Ag NPs at magnification power (10x) were shown in Fig.(2) . The surface image of polymer blend film displayed in part (a) indicates a homogeneous phase without phase separation , in other ward it has finer morphology with smooth surface, showing at this blend

ratio the outstanding miscibility of PVA and PVP . From such figure (part b-f), it can be seen, that ZnO and Ag NPs are well dispersed on the surface of the polymer blend films and this apparent more evident with the increase in the wt.% of Ag. The NCs shows nearly spherical structure of particles of uniform shape. This is because the NPs have a large surface area while the polymeric solution containing different polar groups has a high affinity for ZnO and Ag which leads to the orientation of the nanoparticles within the polymer chain and thus the NC structure becomes more compact and thus the consistency of the material increases. This provided a suitable preparation method for preparing NCs films.
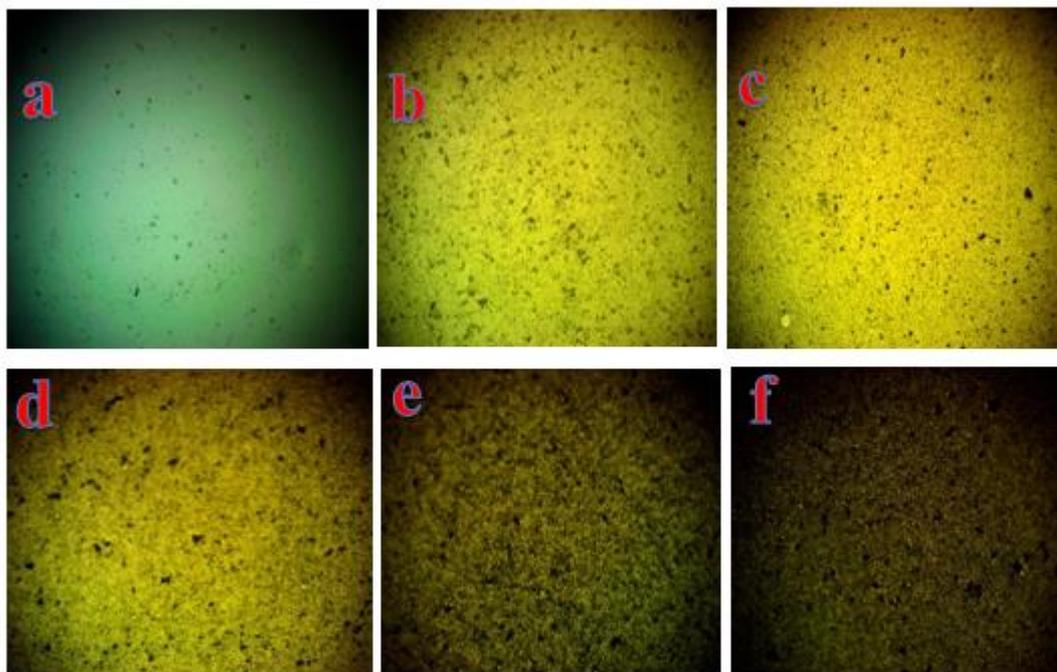
Fig.2: Photomicrographs (10x) for, a. (PVA-PVP) blend, b. (PVA-PVP/ 5wt.% ZnO),   c. 1wt.% Ag, and d. 2wt.% Ag , e. 3wt.% Ag , f. 4wt.% Ag nanocomposite films.

4.3 The Optical Properties

Figure (3) illustrate the UV-Vis-NIR absorption spectra of (PVA-PVP) blend and it's NCs with ZnO and various wt.% of Ag NPs films carried out in the range of 190-1100nm. The absorption edge for NCs films was shifted toward higher wavelength side with adding ZnO and Ag NPs, causing a decrease in the energy gap. This may be attribute to the change in polymeric chain mobility during the blending process. Because of its large energy gap (3.37eV), the most noteworthy attribute of ZnO in the polymer is its effective UV absorption [18]. It can be seen that the absorption of NC is much higher than that of blend. The higher absorption is attributed to the interfacial interaction between the NPs with the adjacent polar groups of blend, which were consistent with reported data[19].
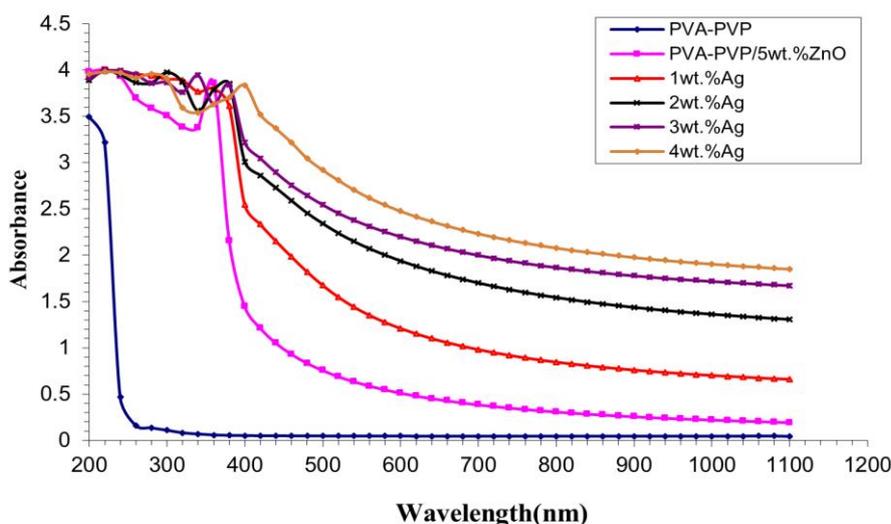
Fig.3 : UV- visible absorbance spectra of (PVA-PVP) and it's NCs with ZnO and different wt.% of Ag NPs.

Optical transmittance spectrum of (PVA-PVP) polymer blend and its NCs with 5wt.% ZnO and different wt.% of Ag films are shown in Fig.(4). The optimal value of transmittance for pure polymer blend is about 98% in the regions Vis and NIR, but it decreases drastically with an increase in the wt.% Ag NPs. This property was due to the nature of the films surface and it's absorption. Reduced the transmittance of the nanocomposite films towards ultraviolet rays qualifies it to use as a packaging for storage drugs regardless of cost.
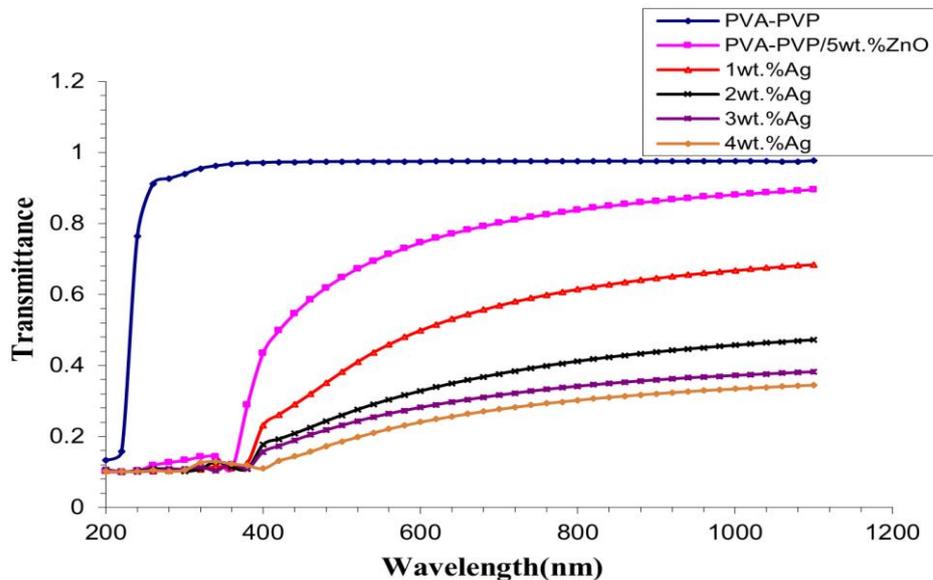
Fig.4: UV-visible transmittance spectra of (PVA-PVP) and it's NCs with ZnO and different wt.% of Ag NPs.

The absorption coefficient (α) of the blended polymers and its NCs films was calculated from Lambert Beer's law [20]:

$$\alpha = 2.303 \frac{A}{t} \qquad (1)$$

Based on the absorption coefficient values of the prepared films ($\alpha < 10^4 \ cm^{-1}$) as in Fig. (5), indirect electronic transitions is extremely likely to occurs. α look smaller at high wavelength, that could related to the little possibility of electron transition. The absorption of the electron is at high energies, which is agree with similar studies of Ag NPs [19].
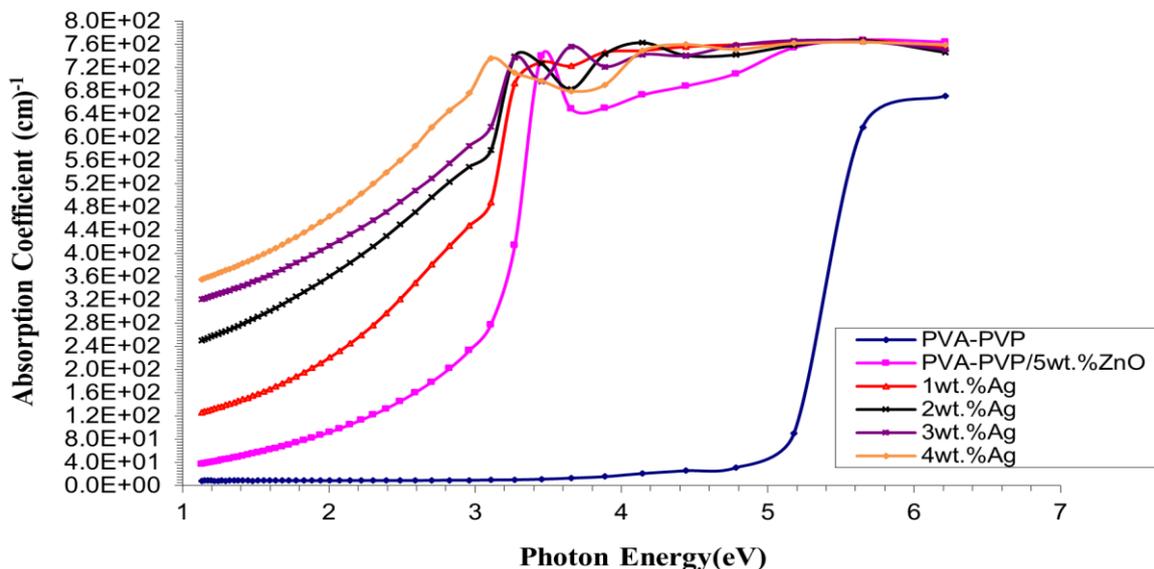
Fig.5: Absorption coefficient of (PVA-PVP) blend and it's NCs with ZnO and different wt.% of Ag NPs.

Depending on the absorption coefficient the optical energy gap can be determined from the plot of $(\alpha h\nu)^{1/r}$ (where r = 2 for allowed and 3 for forbidden indirect transition) versus photon energy (hν) shown in figs. (6) and (7) using the Tauc relation [21].

$$(\alpha h\nu = B \ (h\nu - E_g^{opt} \pm Eph)^r \qquad (2)$$

The both values allowed and forbidden indirect transitions are illustrated in Table (1). It is markedly that indirect E_g^{opt} reduce with additives of ZnO and Ag NPs. This reduce in E_g^{opt} is in good agreement with FT-IR studies and results reported on other polymeric

materials [22]. The presence of silver and zinc ions in the as-prepared films increases the amount of ions available for charge transfer, and defects that lead to the irregular arrangement in the film may increase. Also, these defects create energy states in the energy gap. Hence the increase in the deformation in the polymer matrix improves the conductivity.
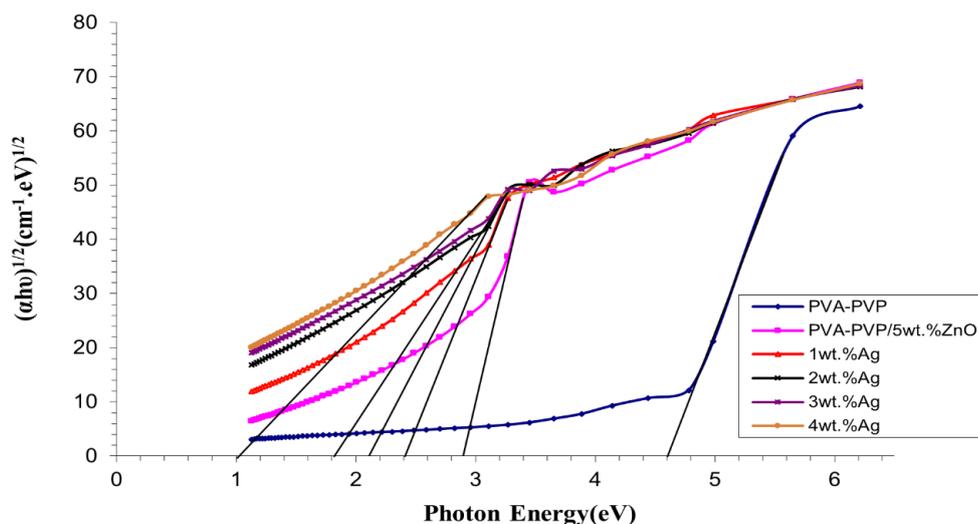
Fig.6: Correlation between $(\alpha h\nu)^{1/2}$ vs. $(h\nu)$ for PVA-PVP blend and its NCs films.
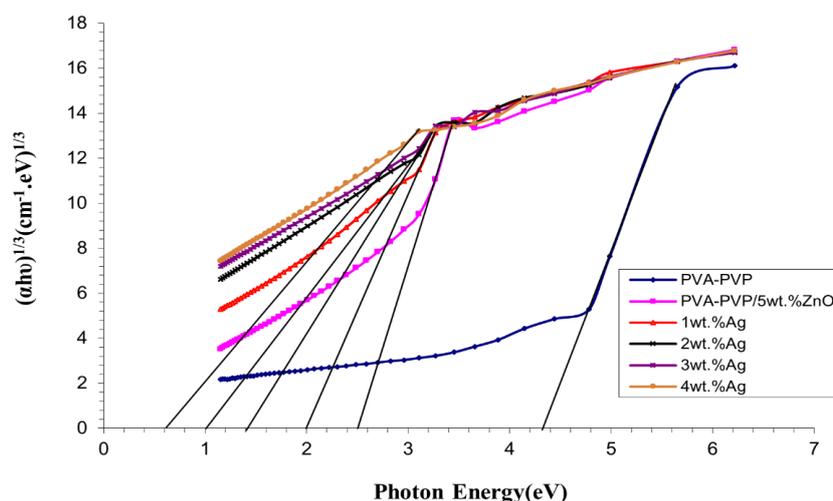
Fig.7:Correlation between $(\alpha h\nu)^{1/3}$ vs. $(h\nu)$ for (PVA-PVP) blend and its NCs films.

Table 2 : E_g^{opt} values for indirect transition of (PVA-PVP) blend and its NCs .

Sample	Allowed (eV)	Forbidden (eV)
PVA-PVP	4.6	4.3
PVA-PVP/ ZnO	2.9	2.5
1wt.% Ag	2.4	2
2wt.% Ag	2.1	1.4
3wt.% Ag	1.8	1
4wt.% Ag	1	0.6

The Refractive Index (n), Polarizibility (P) and Extinction Coefficient (K_O) of pure blend and it's nanocomposites with NPs films has been calculated from the eqs.[23]:

$$n = \frac{1+R}{1-R} + \left[\frac{4R}{(1-R)^2} - K_O{}^2\right]^{1/2} \qquad (3)$$

$$P = \frac{3}{4\pi}\left(\frac{n^2-1}{n^2+1}\right) \qquad (4)$$

$$K_O = \frac{\alpha\lambda}{4\pi} \qquad (5)$$

R is the reflectance.

From the Fig. (8), it was found that the NCs films is bigger than that of pure blend in the Vis and NIR regions of the spectrum, due to the large index of Ag [24] . The decrease in refractive index values at UV region correlates with the behavior of the polarizability below.
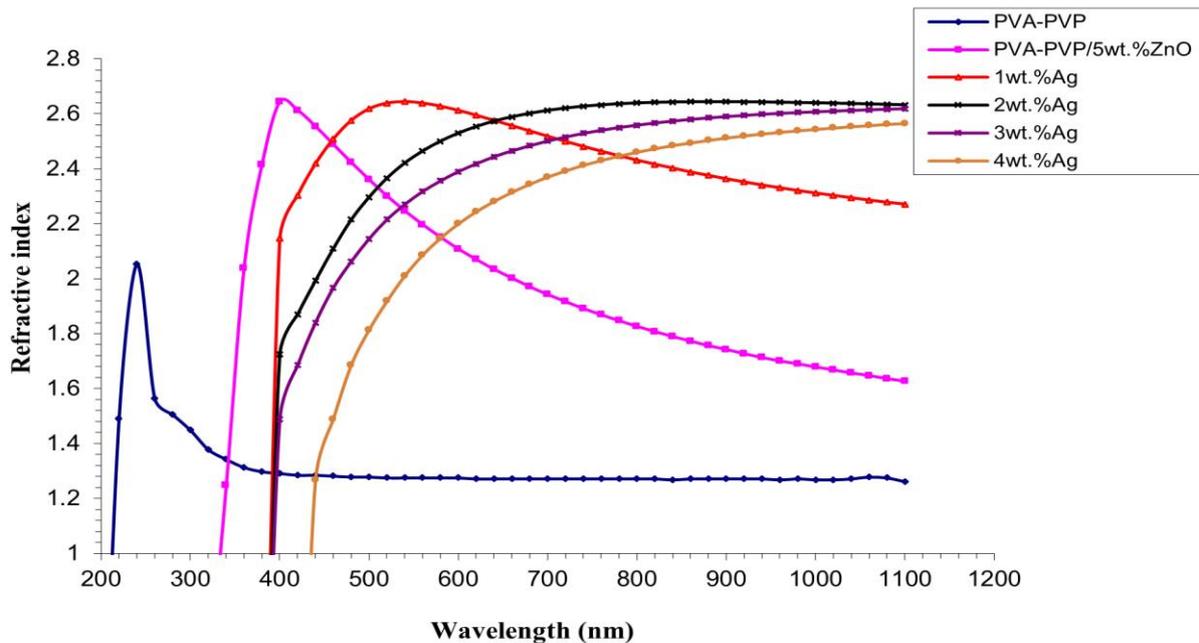
Fig.8: Refractive index (n) of (PVA-PVP) blend and it's NCs films with ZnO and different wt.% of Ag NPs.

From Fig. (9) P curves is identical to that of n , therefor the polarization follows the index of refractive. The refractive index is equal to 1 for materials that don't have any change in the speed of light. The polarizability increases with decreasing $E_g{}^{opt}$ due to the transition of electrons to higher levels , therefore, the strength of its binding to the nucleus is small, therefore P is greater. At UV region, a decrease in the polarization is due to the inability of the dipoles formed to keep up with the high frequency (low wavelength).
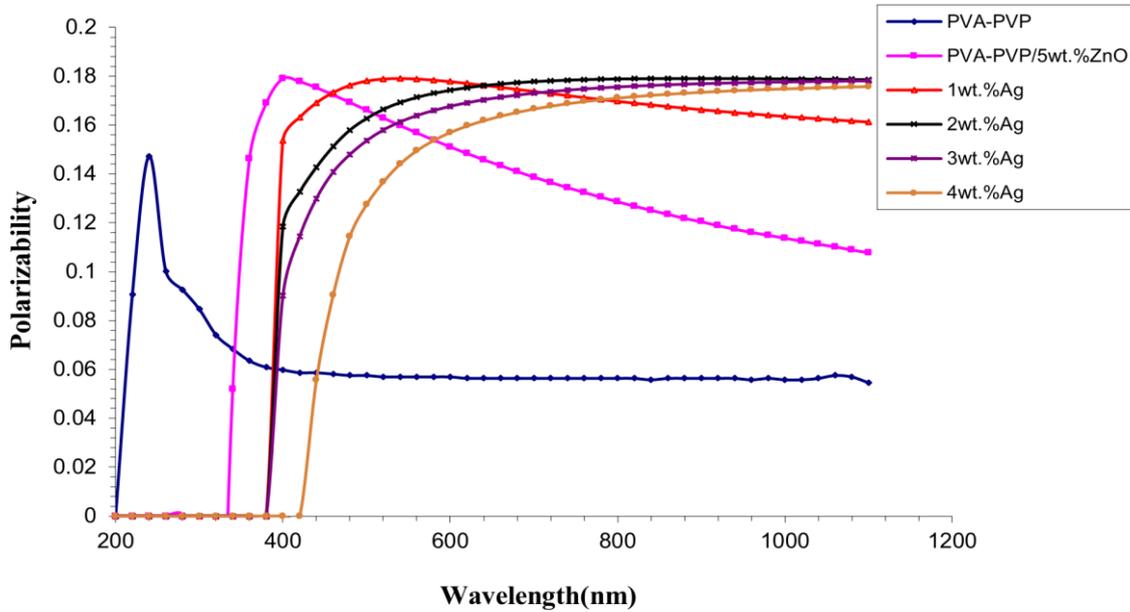
Fig.9: Polarizability (P) of (PVA-PVP) blend and it's NCs films with ZnO and different wt.% of Ag NPs

From observation of the Fig.(10), it can be notice that the extinction coefficient results of the nanocomposites films are much larger than that of the pure polymer blend in all regions. This results was directly depended on the absorption of light .
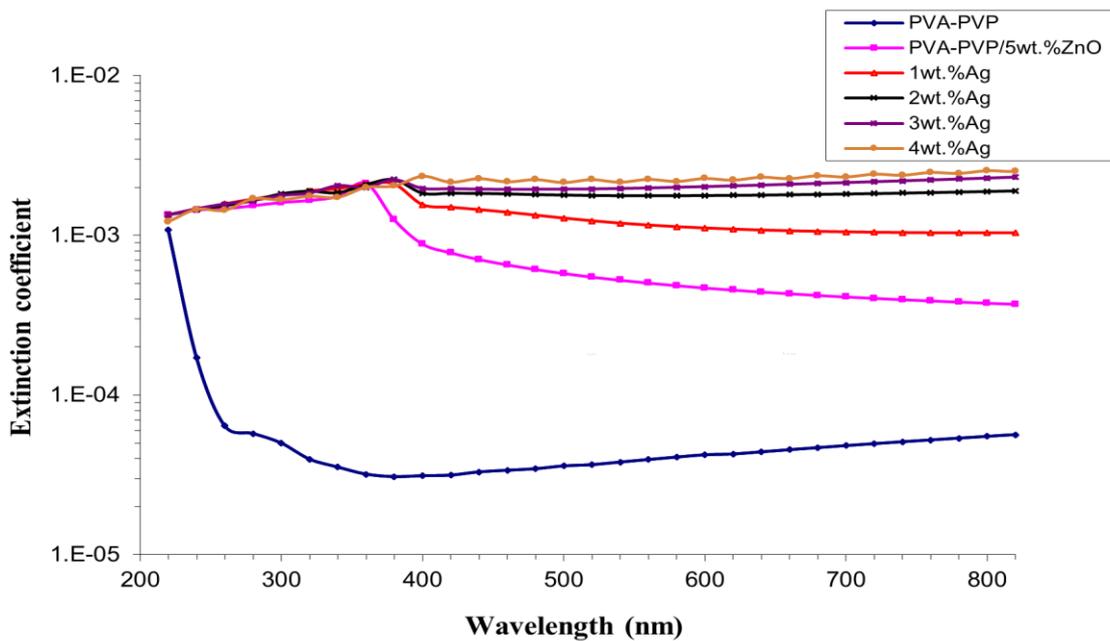
Fig.10: Extinction coefficient of (PVA-PVP) blend and the NCs films .

Conclusions:

The presence of functional groups in polymer NCs systems was verified by FT-IR spectra. Also the transmittance decreases with the increasing ratios of Ag NPs that assigned to increase the density of NPs . The optical microscope photos revealed high homogeneity and fine distribution of ZnO and Ag NPs inside the films. Optimal transmittance value of pure polymer blend is about 98% in the regions Vis and NIR, and the reduced transmittance of the nanocomposites films towards ultraviolet rays qualifies it to use as a packaging for storage drugs regardless of cost.

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