Effect of Nanosilver Particles on the Optical and Structural Properties of (PVA-PVP) Films

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ABSTRACT

In this work,we study the effect of nanosilver particles on optical and structural properties of polymer matrix consisting of polyvinyl alcohol and polyvinyl pyrrolid-one. The samples of (PVA-PVP-Ag) nanocomposites were prepared by using casting method. The weight percentages of nanosilver are (0, 4, 8 , 12 and 16) wt.%.

The experimental results show that the absorbance , the absorption coefficient , extinction coefficient , refractive index and dielectric constant (real, imaginary) are increasing with the increasing of concentrations of the (Ag) nanoparticles, and the energy gap decrease with the increasing of the concentrations of the (Ag)nanoparticles.

We notice through (FTIR) that the (Ag) nanoparticles at films (PVA-PVP-Ag) nanocomposites ,lead to restricted of molecular vibrational motion ,also after addition (Ag) nanoparticles ,some polymer chains have been broken and some other chains have been formed instead.

The SEM shows that (Ag) nanoparticles are randomly distributed in the (PVA-PVP) composites films and it is concluded that small agglomerations is formed in these films

Keywords : Optical Properties , FTIR, Polyvinyl alcohol , Polyvinyl Pyrrolidone , (Ag) nanoparticles.

1. Introduction

Metal nanoparticles combined polymers attracted great consideration because of the widened application goal offered by these hybrid materials [1]. It is well established that polymers, as dielectric materials, are excellent host matrices for encapsulation of metal nanoparticles like silver, gold,copper, and so forth, as they act both as reducing as well ascapping agents and also provide environmental and chemical stability [2]. At the same time, these embedded nanoparticles inside the polymer matrix will also affect the properties of the host itself.Particularly, polymermetal hybrid such as polymer-Ag-nanoparticle composites is promising functional materials in several fields such as optical, electrical, thermal, mechanical, and antimicrobial properties [1]. Many reports in the literature show attempts for synthesis of metal nanoparticles based polymer nanocomposites, with the possibility of variation in their optical and electrical properties for their application in high performance capacitors,conductive inks, and other electronic components .For their application in optoelectronic, electrical, and optical devices, biomedical science, sensors, and so forth, main key points are selection of polymer-metal nanoparticles combination, controlling the particles size, their concentration, and distribution within the polymer matrix [3]. Special worthy has been reached to optical properties of the nanoparticles doped in polymer film, depending on the surrounding medium and on their size, shape, and concentration [4]. Silver nanoparticles have received considerable attention due to their attractive physical and chemical properties and it has been protected by polymers such as PVA, PVP, and PMMA[1]. PVA could be considered as a good hostmaterial for metal due to its excellent thermostability, chemical resistance, high mechanical strength, water solubility, and moderate and dopant dependent electrical conductivity along with its consideration among the best polymers as host matrix for silver nanoparticles [5]. PVA can effectively protect the nanoparticles from aggregation [6].

2.Experimental work

The materials used in this paper are polyvinyl pyrrolidone (PVP) and polyvinyl alcohol as a matrix and nanosilver particle as filler . The polyvinyl pyrrolidone and polyvinyl alcohol (70 wt.% polyvinyl alcohol , 30wt.% polyvinyl pyrrolidone) were dissolved in distill water . The nanosilver was add to the polymer matrix by different weight percentages are (0, 4 ,8, 12 , 16) wt.%. The casting technique was used to preparation the nanocompsites .

The absorption spectrum of (PVA- PVP - Ag) nanocomposites at thickness (0.19,0.17,0.15,0.13,0.11mm) have been recorded in the wavelength range (190-1100) nm by using the double beam spectrophotometer (shimadzu, UV-1800 A°). The absor-ption spectrum have been recorded at room temperature . A computer program was employed to obtain the optical constants, absorption coefficient, extinction coefficient ,refractive index and energy gaps.

The samples (PVA-PVP-Ag) nanocomposites are tested Fourier Transfer Infrared Spectroscopy (FTIR) , by using Vertex 70 from bruker company.

The structural properties of the samples were analyzed by scanning electron microscopy SEM (FEL Quanta 200, Netherlands**)**.

3.Results and discussions

3.1 The absorbance (A)

Figure (1) show the absorption spectrum of (PVA-PVP-Ag) nanocomposites ,as a function of the wavelength of the incident light. It can be noticed from the figures that the absorbance for all films have a high values at wavelength in the neighborhood of the fundamental absorption edge (200nm) , then the absorbance decreases with the increasing of wavelength. These results are in agreement with the researchers [7,8].

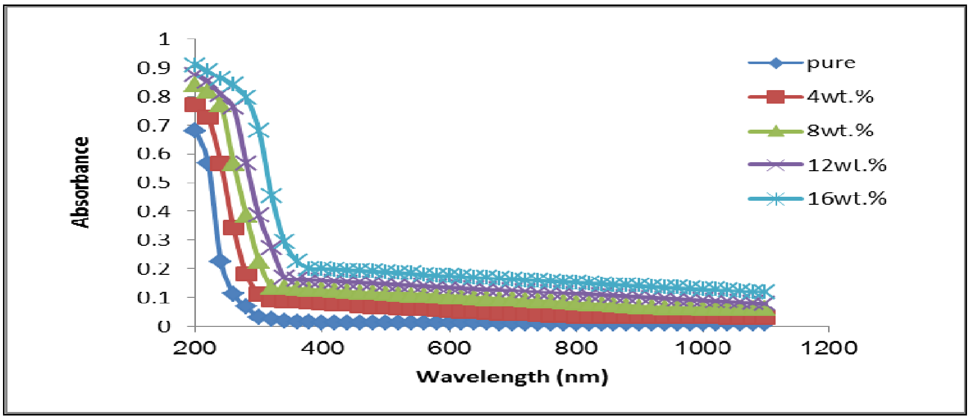

Figure (1) :The absorbance as function of wavelength for (PVA-PVP-Ag) nanocomposites

3.2 Absorption Coefficient (α)

The absorption coefficient $\alpha(cm)^{-1}$ is calculated by using the equation:[9]

$\alpha = (2.303 A) / t_t$

where:(A) absorbance , (t_t)material of thickness .

Figure (2) show the absorption coefficient $\alpha(cm)^{-1}$ as a function of wavelength for(PVA-PVP-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 **(**$h\upsilon < E_g$ **)**.

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 [10] ,among other results is that the coefficient of absorption for the (PVA-PVP-Ag) naoncomposites is less than(10^4)($cm)^{-1}$. These results are in agreement with the researchers [11]

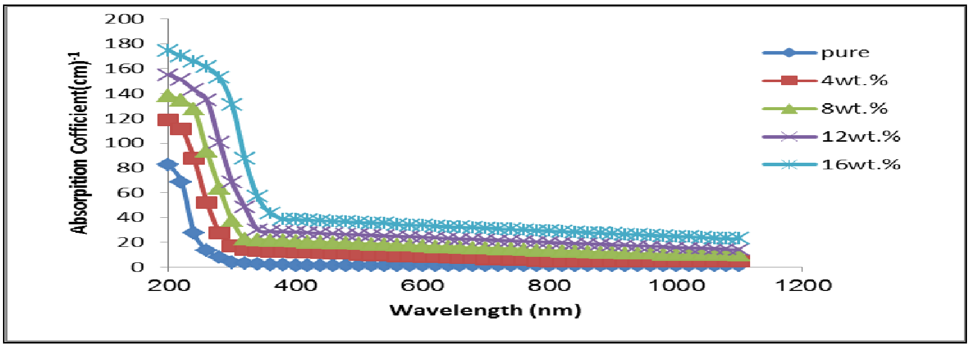

Figure (2): The absorption coefficient α(cm)$^{-1}$ as a function of wavelength(nm) for (PVA-PVP-Ag)nanocomposites

3.3 Energy Gaps of the(allowed and forbidden) Indirect Transition

Both the allowed and forbidden indirect transition band energy gap have been calculated by using the equation[12]:

$$\alpha h\upsilon = B\,(h\upsilon - E_g^{\,opt.} \pm E_{ph.})^r$$

Where: Eph.: energy of phonon, is (-) when phonon absorption, and (+) when phonon emission.

(r = 2) for the allowed indirect transition.

(r = 3) for the forbidden indirect transition.

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 . Figure (3) show the relation between absorption edge (αhv)1/2 for (PVA-PVP-Ag) nanocomposites as a function of photon energy ,on drawing straight line from the upper part of the curve toward the (x) axis at the value (αhv)1/2 =0 we get the energy gap for the allowed indirect transition.We can see that the values of energy gap decrease with the increasing of the weight percentages of silver nanoparticles.

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-PVP-Ag) nanocomposites. Figure (4) show the forbidden transition of the indirect energy gap for the (PVA-PVP-Ag) nanocomposites. These results are in agreement with the researcher [13].

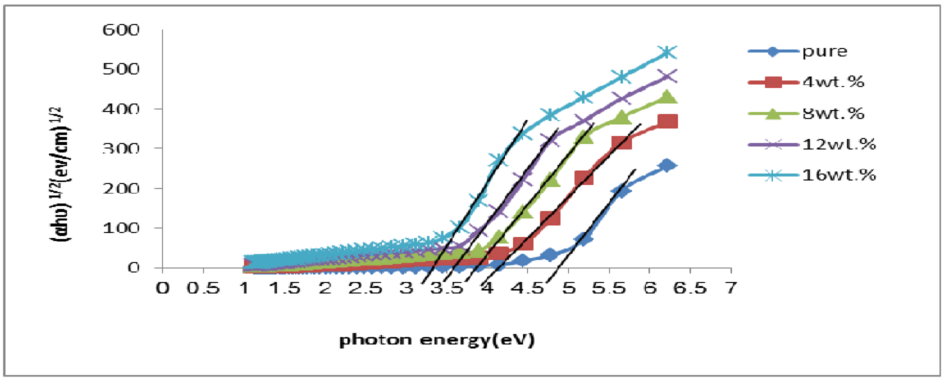

Figure (3):The energy gap for the allowed indirect transition(αhυ)$^{1/2}$ as a function of photon energy of (PVA-PVP-Ag) nanocomposites.

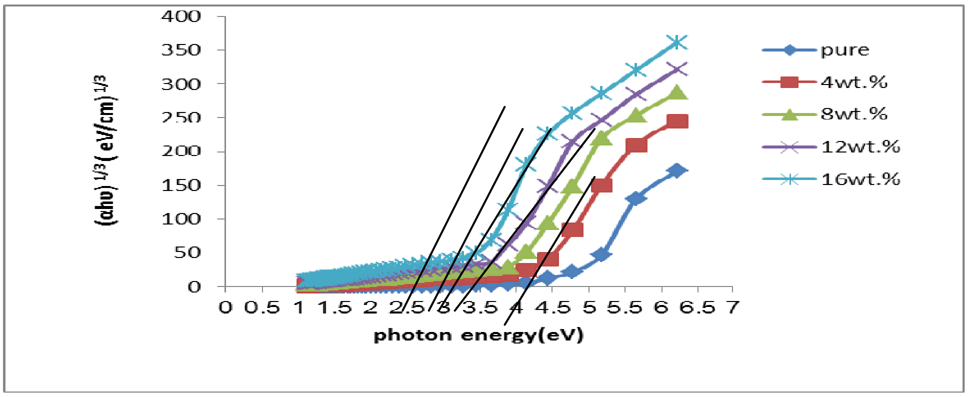

Figure (4):The energy gap for the forbidden indirect transition$(\alpha h\upsilon)^{1/3}$ as a function of photon energy of (PVA-PVP-Ag)nanocomposites.

3.4 Refractive Index

The refractive index is calculated from the equation:[14]

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

Where:(n) Refractive Index ,(R) Reflectance ,(k) Extinction Coefficient.

Figure (5) show the change of refraction index for (PVA-PVP-Ag) nanocompos-ites as a function of wavelength . From the figures we can see that the refractive index increases with increasing the weight percentages of the concentration of nanoparticles (Ag) to(PVA-PVP). The reason of this result is, the increase of the (Ag) concentration leads to increase the density of the nanocomposites . These results are in agreement with the researchers [8].

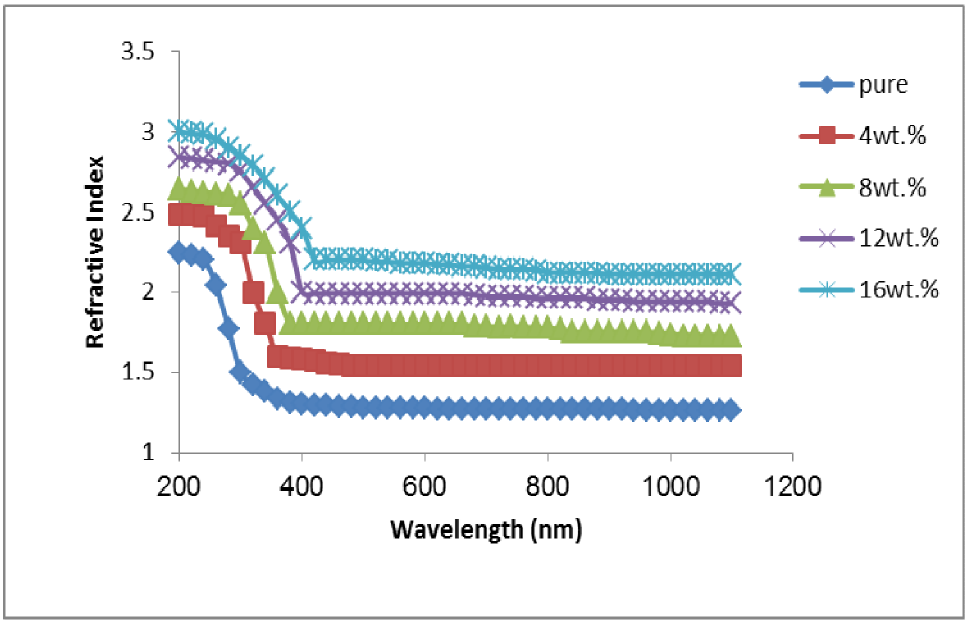

Figure (5):The refractive index(n)as a function of wavelength for (PVA-PVP-Ag) nanocomposites

3.5 Extinction Coefficient(k)

Extinction coefficient (k) is calculated by using the equation:[15]

$$k = \alpha_{op} \lambda / 4\pi$$

Where λ : is the wavelength of incident photon rays.

The change of the extinction coefficient as a function of the wavelength is shown in figure (6) for (PVA-PVP-Ag) nanocomposites .It can be noted that (k) 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.

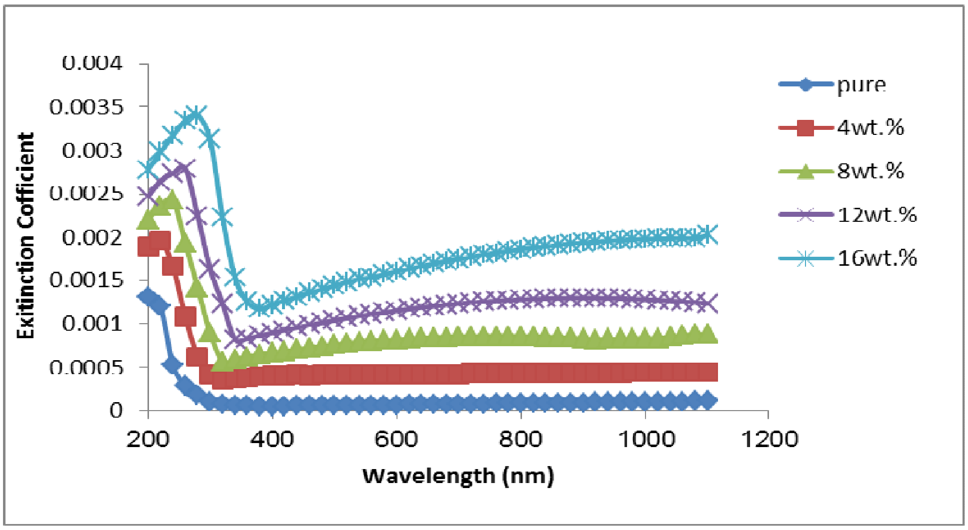

Figure (6):The Extinction coefficient as a function of wavelength for (PVA-PVP-Ag) nanocomposites

3.6 Real and Imaginary part of Dielectric constant

The real and imaginary dielectric constant (ε_1,ε_2) for (PVA-PVP-Ag) nanoc-omposites have been calculated respectively from the equations:[12]

$$\varepsilon_1 = n^2 - k^2$$

$$\varepsilon_2 = 2n\,k$$

The figure (7) show the change of (ε_1) as a function of the wavelength . It can be seen that(ε_1)considerably depends on (n^2) due to low value of (k^2) so, the real dielectric constant is increased with the increase of the concentrations of (Ag) nanoparticles . Figure (8) show the change of (ε_2) as a function of the wavelength .It can be seen that (ε_2) is dependent on(k) values that change with the change of the absorption coefficient due to the relation between (α) and (k).

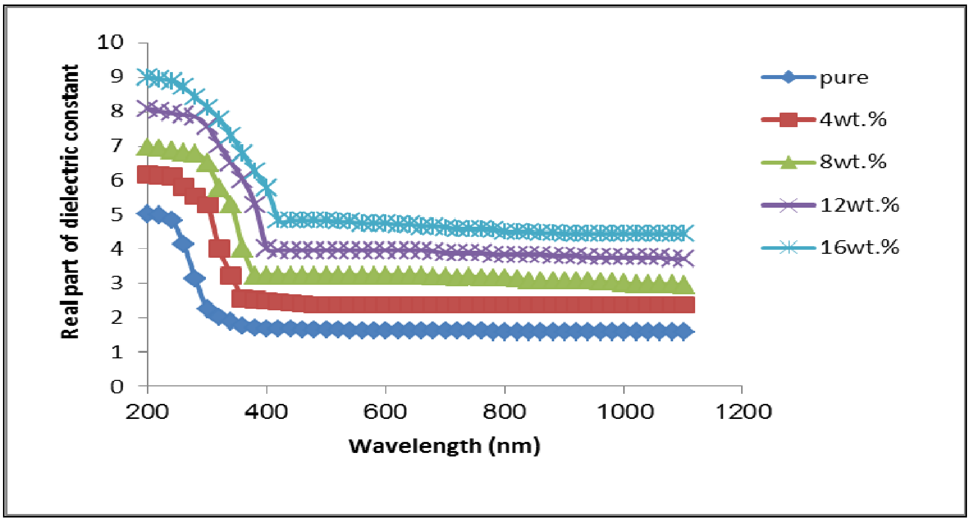

Figure (7):The real dielectric constant(ε_1) as a function of wavelength for (PVA-PVP-Ag) nanocomposites

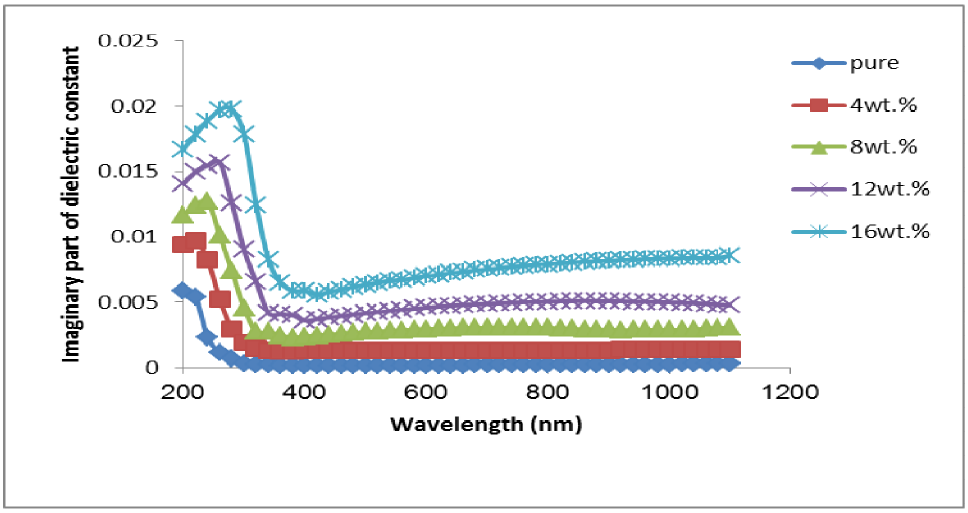

Figure (8):The imaginary dielectric constant(ε_2) as a function of wavelength for (PVA-PVP-Ag) nanocomposites

The microscopic photographs in figure (9) taken for samples of different concentrations at magnification power(100x). However, when the concentration reaches to 16wt.% for(PVA-PVP-Ag) nanocomposites, the nanoparticles form a continuous network inside the polymer . These results are in agreement with the researcher [13].

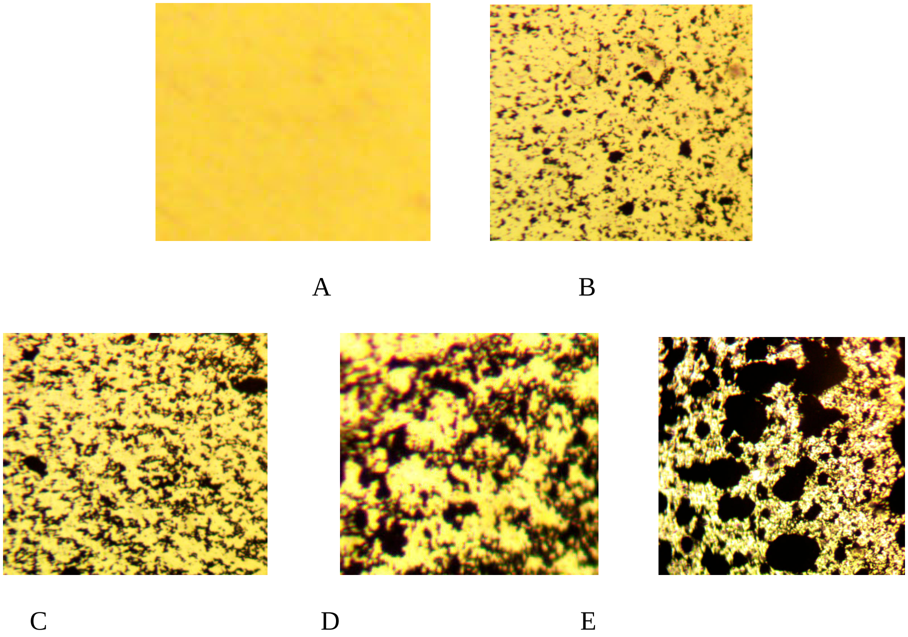
A B
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Figure (9) :Photomicrographs for (PVA-PVP-Ag) nanocomposites
(A) for pure,(100x) , (B) for 4wt.% Ag ,(100x),(C) for 8wt.% Ag ,(100x),
(D) for 12wt.% Ag ,(100x),(E) for 16wt.% Ag ,(100x).

3.7 FTIR Measurements

The fourier transform infrared spectroscopy (FTIR) spectra of pure (PVA-PVP) composite as shown in figure (10) and add concentration (Ag) nanoparticles to the films are shown in figures (11-14) .All spectra exhibit the characteristic absorption bands of pure (PVA-PVP) composite , which are (3271.35,2921.96,1650.94,1493.12-1141.76 , 1089.61) cm^{-1} .

It can be noticed that these treatment cause some observable changes in the specral features of the samples a part from new absorption bands and slight changes in the intensities of som absorption bands.

The new bands may be correlated likewise with defects induced by the change transfer reaction before the polymer chain and the dopant.

The vibrational peaks at (3271.35,2921.96,1650.94,1493.12-1141.76 , 1089.61) cm^{-1} are assigned to O-H stretching,C-H stretching,C= O stretching,C= C stretching ,and C-O-C rocking of (PVA-PVP) composite respectively as shown in figure (10).Further, the vibrational peaks found in the range (642.97-1650.94) cm^{-1} may be attributed to (Ag) nanoparticles , which indicate that (Ag) nanoparticles doped in the (PVA-PVP) composite.

The experimental data given the figures (11-14) after addition (Ag) nanoparticles ,some polymer chains have been broken and some other chains have been formed instead.

We notice through (FTIR) if presence (Ag) nanoparticles at films (PVA-PVP-Ag) nanocomposites ,lead to restricted of molecular vibrational motion, and special vibrational motion at three dimension for (PVA-PVP) composite and most probably be affected of IR energy and this restricted of molecular polymers move reason occurrence apparent distortion for some the parts functional for polymers (functional groups) ,therefore that films nanocomposites has characteristic nano approximately being restricted or assemble all functional groups for polymer when apparent at IR[16] as shown in figures (11-14). These results are in agreement with the researchers[17].

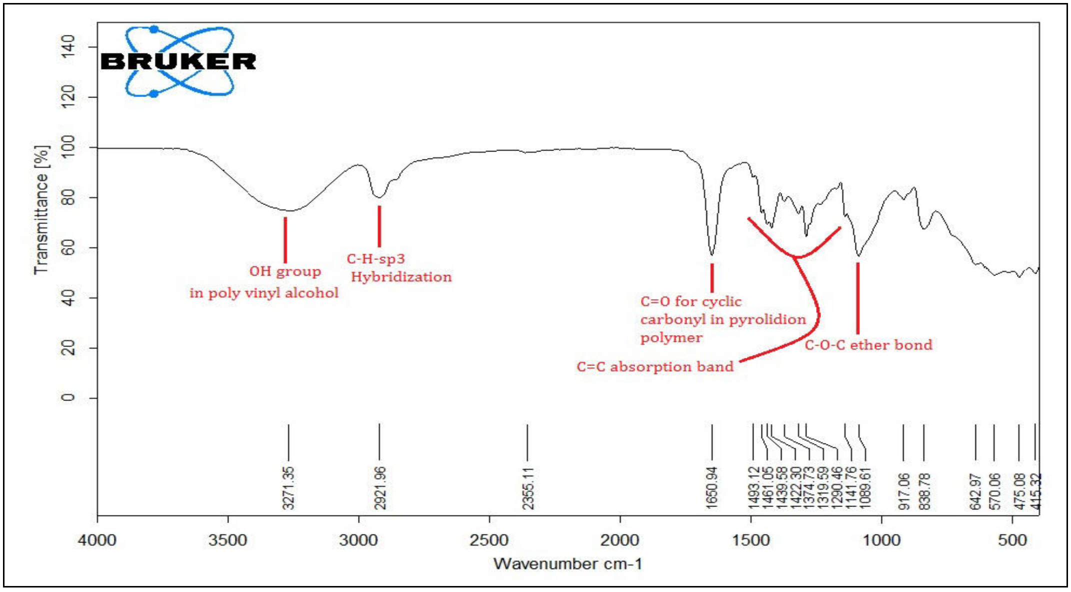

Figure (10):FTIR for (PVA-PVP-Ag) Nanocomposites for pure

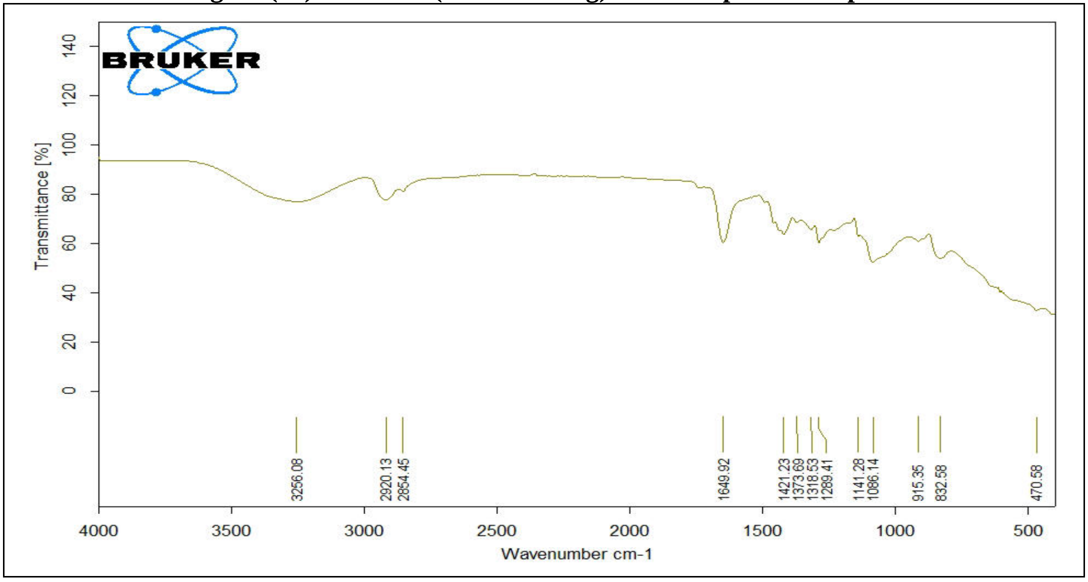

Figure (11):FTIR for (PVA-PVP-Ag) Nanocomposites for (4wt.%)Ag

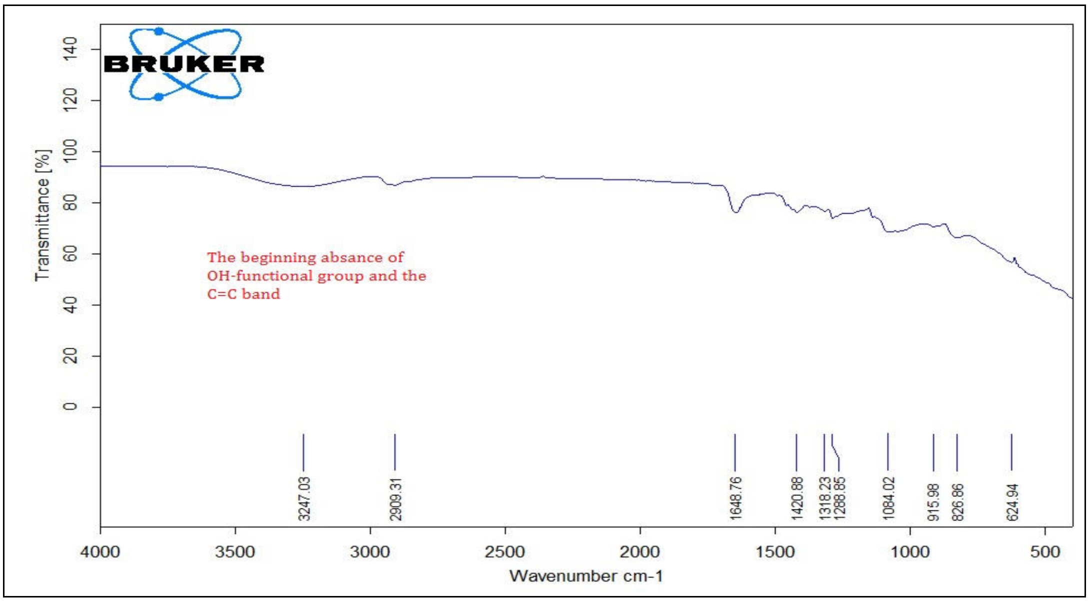

Figure (12):FTIR for (PVA-PVP-Ag) Nanocomposites for (8wt.%)Ag

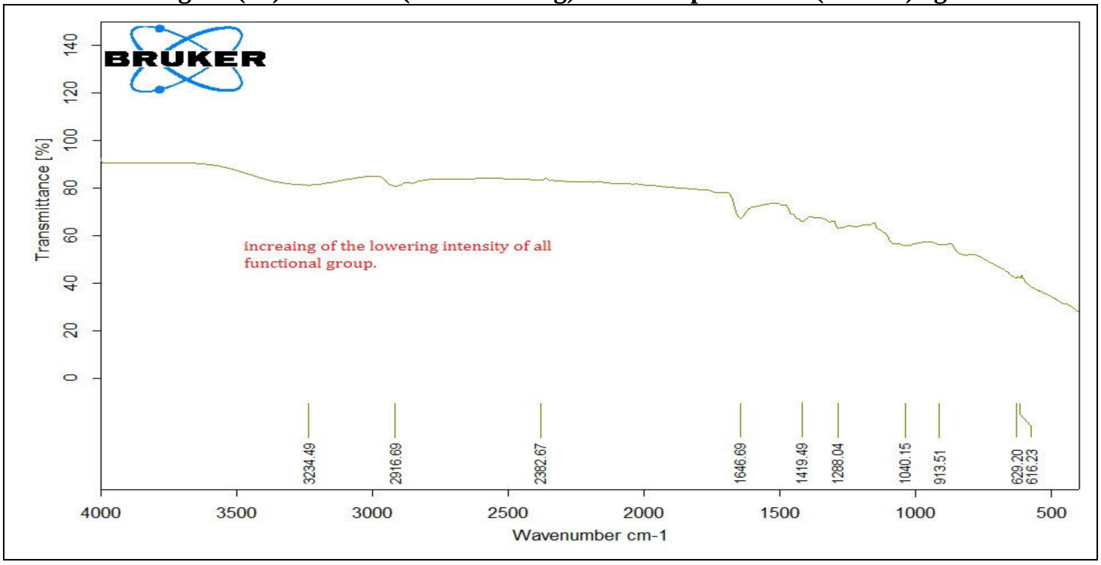

Figure (13):FTIR for (PVA-PVP-Ag) Nanocomposites for(12wt.%) Ag

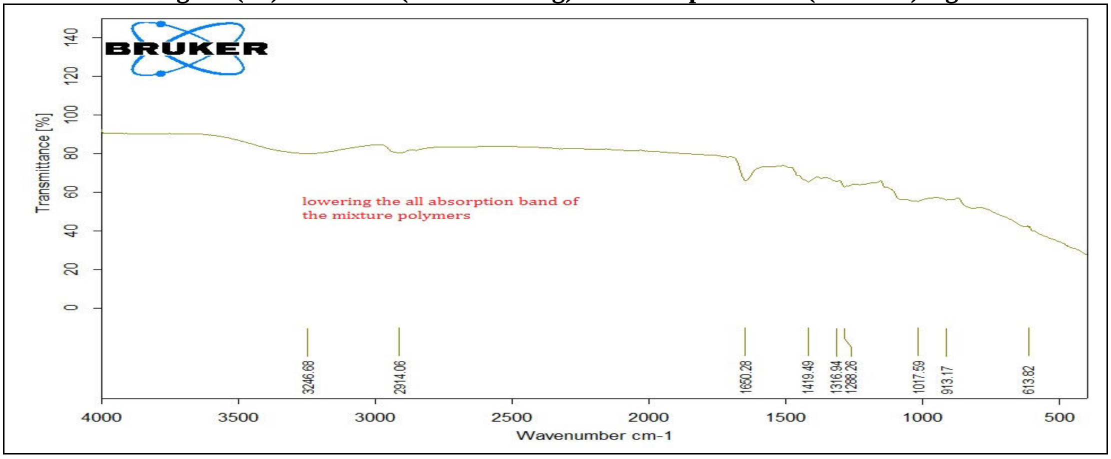

Figure (14):FTIR for (PVA-PVP-Ag) Nanocomposites for (16wt.%)Ag

3.8 SEM Measurements

The SEM shows the very detailed three dimensional images at very high magnification.

The surface structure of (PVA-PVP) and (PVA-PVP-Ag) can be imaged through SEM with high clarity.

SEM images depict the surface morphology of (PVA-PVP-Ag) nanocomposites before and after addition concentration of (Ag) nanoparticles which are shown in figure (15) the films exhibit uniform density of grain distribution at surface morphology.

The surface morphology of (PVA-PVP-Ag) nanocomposites films show many aggregates or chunks randomly distributed of (Ag) nanoparticles on the top surface of the films.

The results indicate that the (Ag) nanoparticles tended to form aggregates and good dispersed at (PVA-PVP) composites films.

From the figure (15) it is absorbed that, (Ag) nanoparticles are randomly distributed in the (PVA-PVP) composites films and it is concluded that small agglomerations is formed in these films[18]. These results are in agreement with the researchers[19].

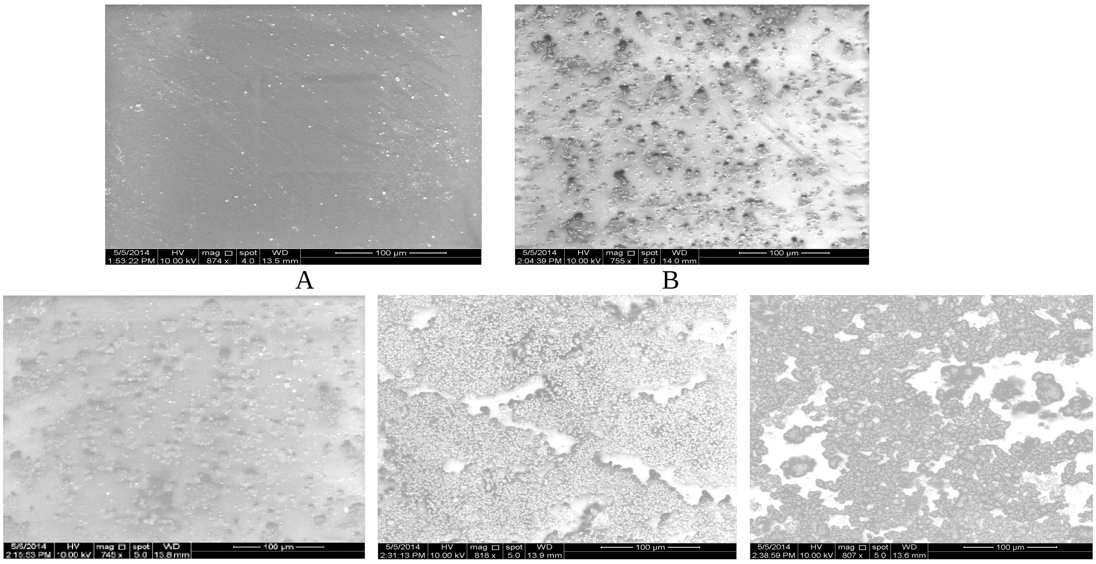
A B
C D E

Figure (15) : SEM images for (PVA-PVP-Ag) Nanocomposites (A) for pure,(B) for 4wt.% Ag, (C) for 8wt.% Ag , (D) for 12wt.% Ag, (E) for 16wt.% Ag

4. Conclusions

The summarized results from this work are the following:

1. The absorbance and the absorption coefficient for (PVA-PVP-Ag) nanocomposite increases with the increasing of the concentrations of the (Ag) nanoparticles.
2. The absorption coefficient (PVA-PVP-Ag) nanocomposites is less than $(10^4)(cm)^{-1}$.
3. The energy gap of the transitions decreases with the increasing of the concent-rations of the (Ag)nanoparticles.
4. Extinction coefficient , refractive index and dielectric constant (real, imaginary) are increasing with the increasing of concentrations of the (Ag)nanoparticles.
5. The (Ag) nanoparticles at films (PVA-PVP-Ag) nanocomposites ,lead to restricted of molecular vibrational motion ,also after addition (Ag) nanoparticles ,some polymer chains have been broken and some other chains have been formed instead.
6. The SEM shows that (Ag) nanoparticles are randomly distributed in the (PVA-PVP) composites films and it is concluded that small agglomerations is formed in these films.

5. References

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