Optical and morphological properties of (PMMA -Ag) nanocomposites

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ABSTRACT

Polymer-nanoparticale composites were prepared by solution cast method using Polymethylmethacrylate as base matrix and silver nanoparticle as filler. Optical properties of (PMMA-Ag) nanocomposite with different percentage (0,2,4,6, 8,10)wt% and thickness 100μm are investigated using uv-visspectroscopy within the spectral region (200-800)nm. The energy gap of indirect transition (allowed and forbidden) has been determined and it was decreased with increasing nanoparticles concentration. The dispersion phenomena for refractive index and extinction coefficient are also investigated, the refractive index increase with increasing Ag concentration. The morphological analysis of the samples is determined by AFM measurements and optical microscope. The result shows a homogeneous distribution,very smooth surface and small roughness.   © 2014 Trade Science Inc. - INDIA

INTRODUCTION

In recent years, a noble metal nanoparticles such as silver is of great significance due to size dependent optical properties[1]. These special and unique properties could be attributed to their small sizes and large specific surface area. The metallic nanoparticles have been used in many applications such as catalysis, electronics and photonics. Polymers are considered to be an excellent host material for nanoparticles of metals[2]. The polymer will act as a surface capping agent when the nanoparticles are embedded into them. The obtained nanocomposites might exhibit enhanced optical properties[3]. However, the properties of polymer composites depend on type of incorporated nanoparticles, as well as their size and shape, concentration and interaction with the polymer matrix. Among polymer materials, PMMA is well known as a polymeric glass with a wide range of applications. Use of PMMA offers two fold advantages such as availability to carboxylate functional group for a chemical bonding with the metalions

and high solubility of PMMA in solvent like Chloroform for silver nitrate reduction. Various preparation routes have been reported for the preparation of metallic nanoparticles; including reverse micelles process[4,5], salt reduction[6], ultrasonic irradiation[7], electrochemical synthesis[8,9] and etc. Deng et al.,[10] prepared PMMA-Agnanocomposites by considering silver nanoparticles colloids suspension drying on the quartz substrates using PMMA and DMF via in-situ technique. They observed that the behaviors of linear and nonlinear optical properties were different compared to the pure PMMA film. In this paper, we used simple procedure for preparation of PMMA/ Agnanocomposites with ahomogeneous distribution of metal nanoparticles in the polymer matrix without using any external reducing agent. The insitu produced Ag+ ions were bound to the acrylate polymer through a chemical bonding which later helps the Ag+ ions to get converted into the Ag.
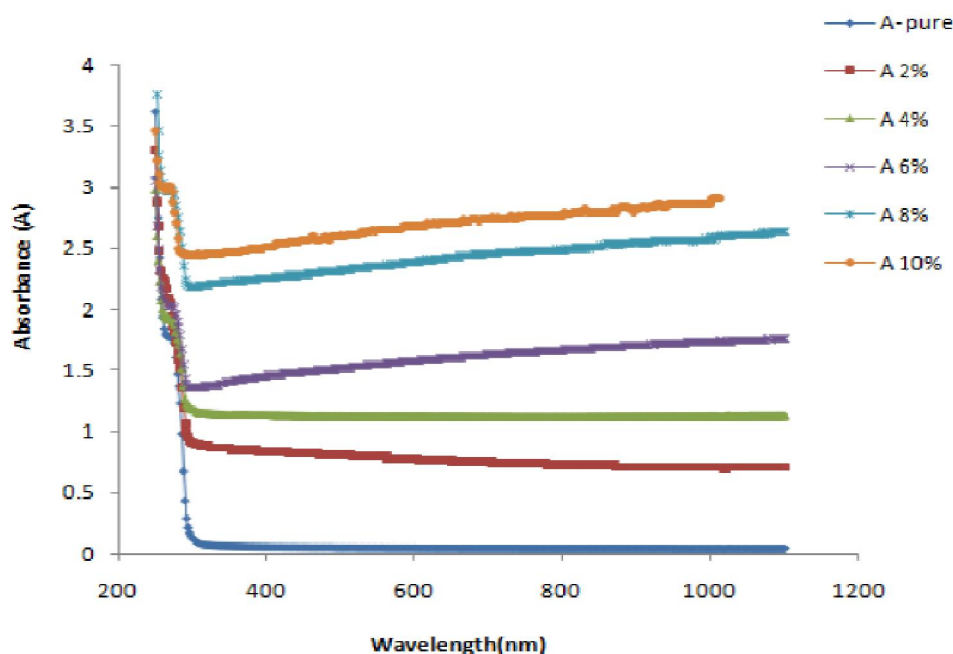
EXPERIMENTAL MATERIALS

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Figure 1 : The absorbance for (PMMA-Ag) composites as afunction of wavelength.

The materials used in this work are commercial Polymethylmethacrylate (PMMA), it was obtained as fine powder Netherland company and Silvernanopowder Black Color Size (20nm) with apurity (99.99%) supplied from (Hongwu nanometer).

Films were prepared with weight percent (2, 4, 6,8 and 10wt%). It was dissolved in Chloroform using magnetic stirrer about (1hr). The process of sonicacation is one that shoots ultrasonic waves at the sample ;therefore aiding dispersion of the filler and creating a more homogenous solution, so to prepare the filmsEach sample is poured in 5×5 cm^2 glass basin after been cleaned with water and acetone. They are keptto Placed on a flat table surface. The thickness of the dried samples is about (100μm).

RESULTS AND DISCUSSION

Optical properties

The UV-VIS absorbance spectra in the region 200–800nm for PMMA-Ag nanocomposites are shown in Figure 1. It isclear from the figure that the absorption spectra for all films decreased with increasing wavelength, while the absorption increased with increasing concentration of Ag. This is because silver nanoparticles ions are combined with the polymer chains which absorb the incident radiation at the shortest wavelengths

greater than 250 nm by the free electrons [11,12].

The optical transmission spectra of the PMMA films with different concentrations ofnano Ag are shown in Figure 2. This figure shows that the transmittance intensity increases with the increasing of the wavelength, and as the concentration of nano Ag increases, the transmittance decreases. The reason for this behavior is because of the form of covalent bonds between polymer chains and additives that decrease the transmitting of the incident light especially at the shortest wavelengths. The electrons in the outer orbits have travelled to the higher energy levels and have occupied vacant positions of energy bands. Thus, part of incident light does not penetrate through it[12]. However, the pure Polymethylmethacrylate have no free electron and the conductionband needs photon with high energy as shown in the Figure 2.

The absorption coefficient α(cm)$^{-1}$ is calculated by using equation (1).

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

where (A) is the absorbance and (t) is the thickness of the matter.

Figure 3 shows the absorption coefficient α(cm)$^{-1}$ as a function of wavelengthAt low energies, the possibility of electron transition is little, because the energy is not sufficient to move this electron from the valence band to the conduction band (hυ<Eg)[11]. At high ener-
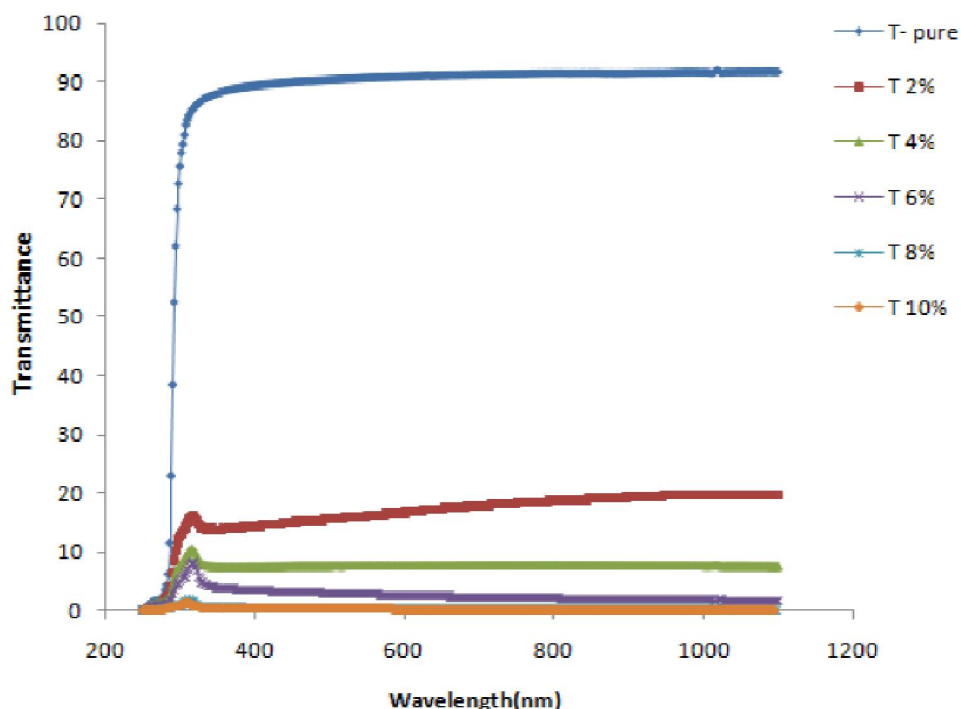
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Figure 2 : The transmittance for (PMMA-Ag) composites as a function of wavelength.
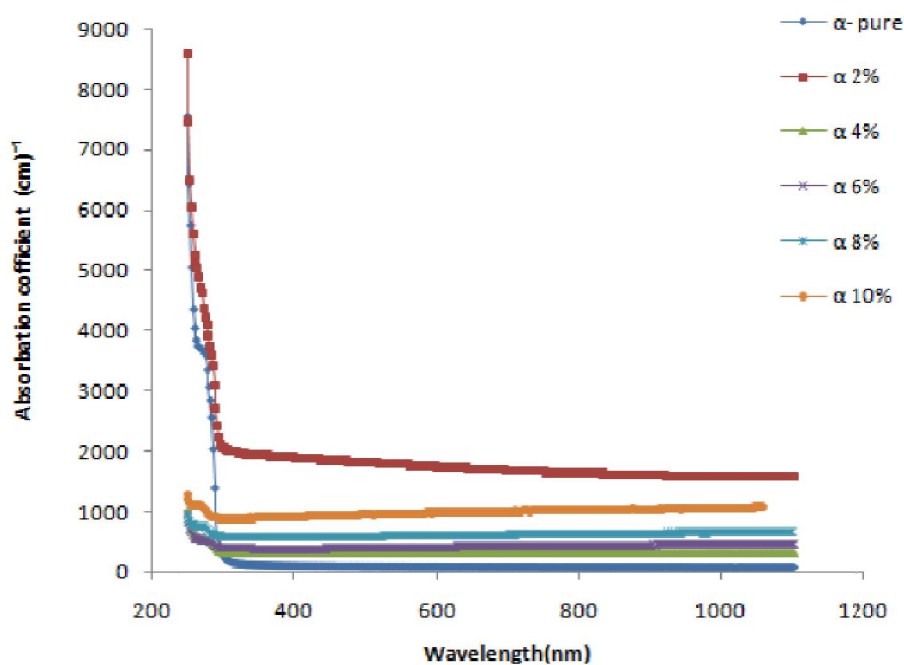

Figure 3 : The absorption coefficient for (PMMA-Ag) composites as afunction of wavelength.

gies, absorption is great,this means that a great possibility of electron transitions consequently, the energy of the 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 energy gap[12]. This shows that the absorption coefficient assists in figuring out the nature of electron transition,[13],among other results is that the coefficient of absorption for the (PMMA-Ag) composites is less than $10^4 cm^{-1}$ thismeans transitions is indirect.

Refractive index (n) was determined from the absolute values of the absorbance and transmittance of the investigated films using the following equation [2]:

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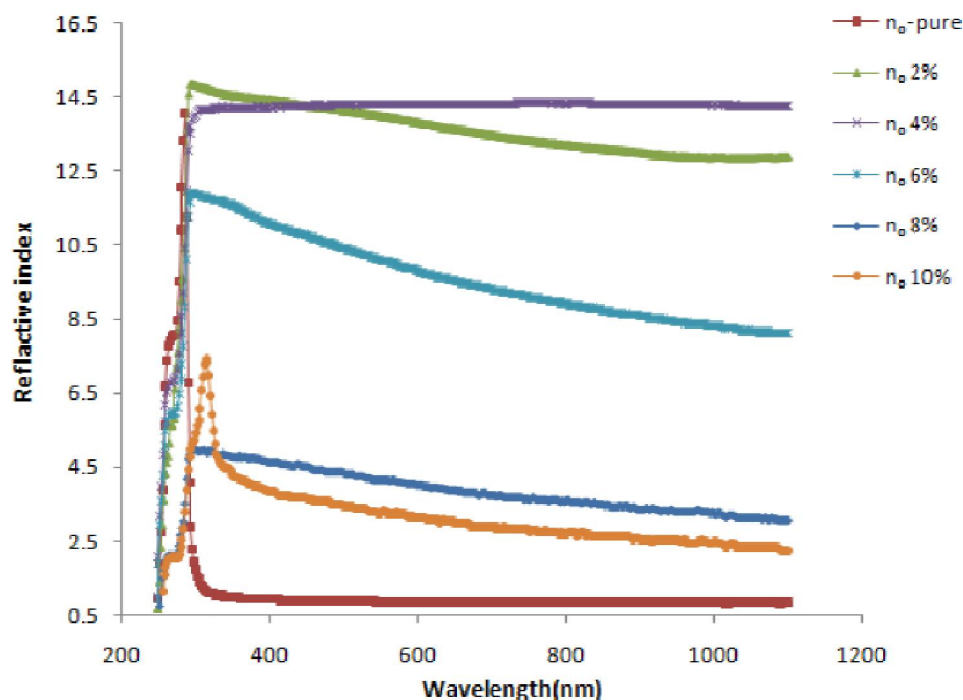Polymer

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Figure 4 : The refractive index for (PMMA-Ag) composites as a function of wavelength.

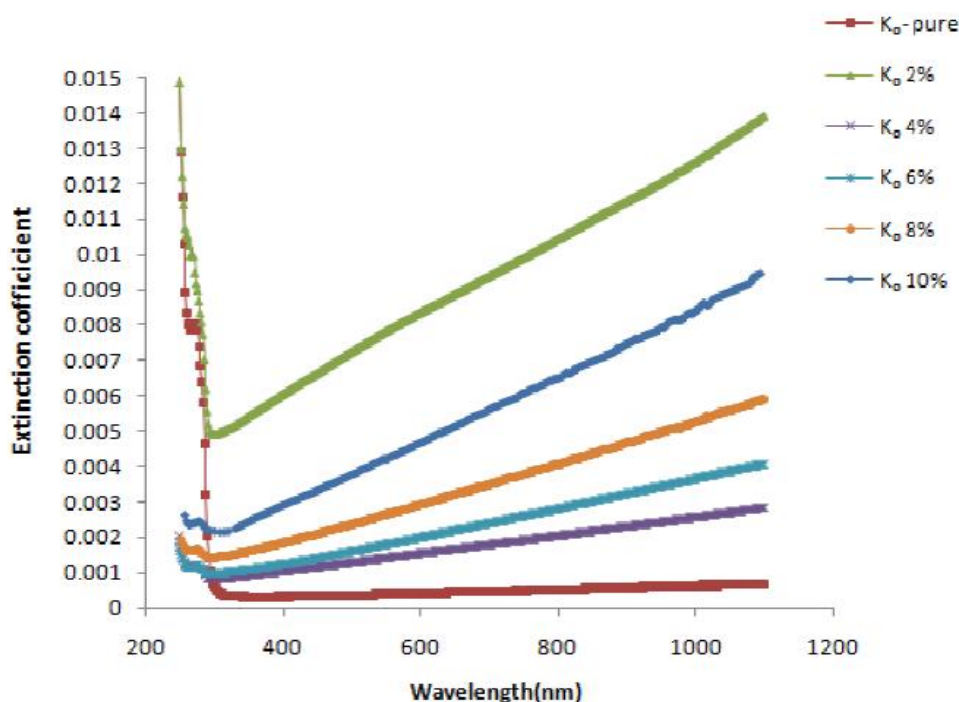**Figure 5 : The extinction coefficient for (PMMA-Ag) composites asafunction of incident wavelength.**

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

where R is the optical reflectance. Figure 4 represents the dispersion in the refractive index for the films in the investigated range of wavelengths. Inspection of Figure 4 indicates that the refractiveindex decreases with increasing wavelength for samples pure, 2, 6, 8 and 10% but sample 4% increase with wavelength. The figure shows that the refractive index increases as a result of an increase in the percentage of Ag; this behavior can be attributed to the increasing of the packing density as

a result of filler content[14].

The extinction coefficient was determined using the following equation (3).

$$K = \dfrac{\alpha\lambda}{4\pi} \qquad (3)$$

where α is the absorption coefficient and (λ) is the wavelength of the incident ray.

In Figure 5,it is clear that the extinction coefficient for pure PMMA sample shows a decrease in values of all wavelengths (200–800) nm, while it increases for the samples (2, 4, 6, 8, and 10%), in the wavelength from 300 nm to 800 nm. Extinction coefficient was increased for PMMA films with increasing Ag concentration, this may be attributed to high absorption coefficient. This result indicates that the atoms of (Ag) will modify the structure of the host polymer. An interesting result is silver nanoparticles increases the absorbance in the visible region[15].

The dependence of the real part is shown in Figure 6 for pure sample and with Ag nanoparticles. It was observed that the real part depends on refractive index. The real part is increased with increasing wavelength and Ag concentration, moving the curve vertex to higher wavelengths were noticed with increasing Ag nanoparticles percentage may be attributed to related real part of dielectric constant with refractive index by

equation (4)[16].

$$\varepsilon_1 = n^2 - k^2 \qquad (4)$$

$$\varepsilon_2 = 2nk \qquad (5)$$

where (α) is the complex dielectric constant, (α_1, α_2) are the real and imaginary parts of the dielectric constant, respectively.

The imaginary part of the dielectric constant as a function of wavelength is shown in Figure 7. It is clear that the imaginary part depends on extinction coefficient by equation 5 because therefractive index is very small[16,17].

The imaginary part increases for all wavelengths 200nm to 800 nm and with increasing Ag percentage. New peaks appear which indicate that the samples have no same structure. Hence, the change in the percentage of Aggave change in the chemical composition of the polymer[18]. The absorption spectra clarify an extending tail for lower photon energies below the band edge,[19].

Figure 8 shows the relation between $(\alpha h\nu)^{1/2}$ for (PMMA-Ag) composites as a function of photon energy on drawing a straight line from the upper part of the curve toward the (x) axis. At the value $(\alpha h\nu)^{1/2} = 0$ we get an energy gap for the allowed indirect transition. The obtained values are shown in TABLE 1. We can
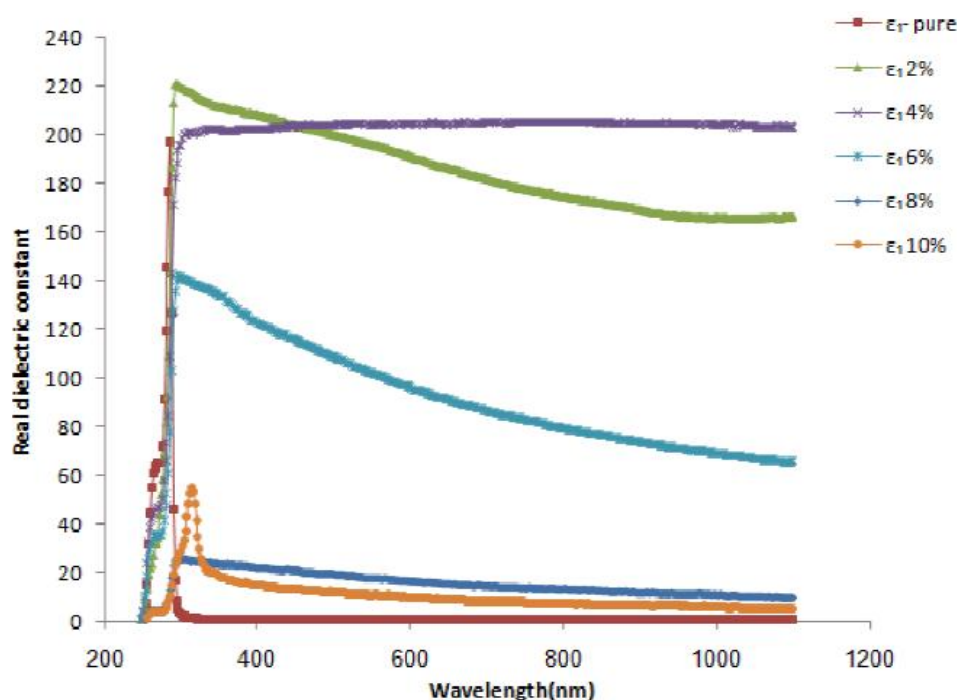

Figure 6 : The real dielectric constant for (PMMA-Ag) composites as a function of wavelength.
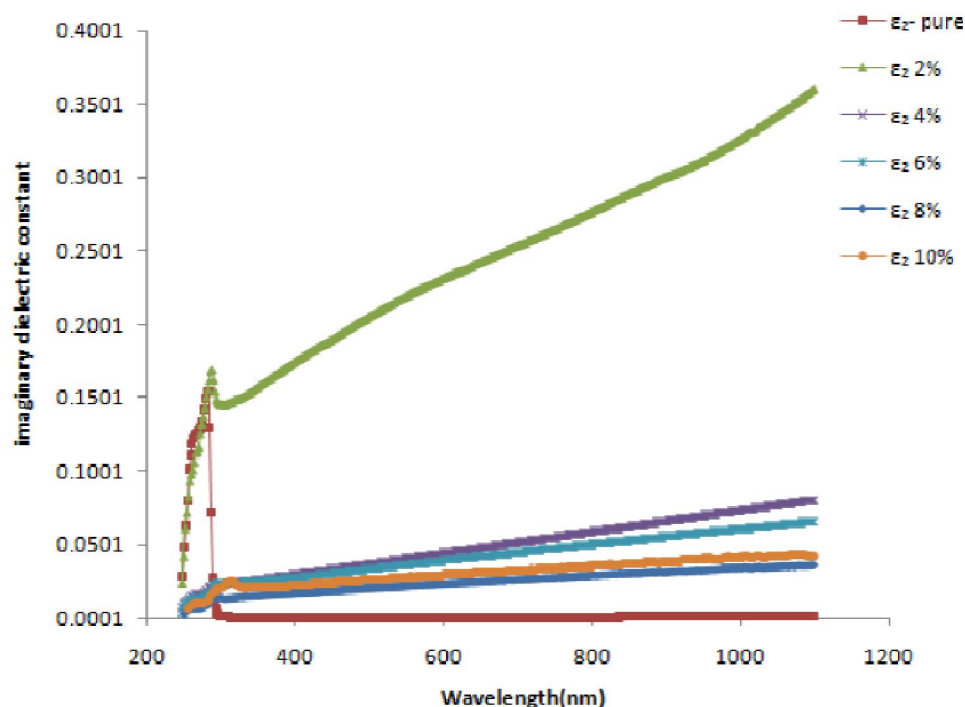
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Figure 7 : The imaginary dielectric constant for (PMMA-Ag) composites as a function of wavelength.

TABLE 1 : The values of energy gap for the allowed and forbidden indirect transition

Ag Wt%	Allowed $(\alpha E)^{1/2}$		Forbidden $(\alpha E)^{1/3}$	
	E_{g1}	E_{g2}	E_{g1}	E_{g2}
0	4.3	4.9	4.3	4.91
2	4.2	4.8	4.2	4.8
4	4.1	4.7	4.07	4.7
6	4	4.6	4	4.6
8	3.7	4.4	3.8	4.4
10	3.3	4	3.5	4.1

TABLE 2 : Values (RMS) and (RS) and (Avg. Diameter) for samples

wt%	RMS(nm)	Roughness(nm)	Avg.Di(nm)
0	0.22	0.18	95.99
2	0.05	0.04	107.74
4	0.46	0.38	102.91
6	0.48	0.39	100.3
8	0.23	0.18	88.84
10	2.48	2.06	106.2

see that the values of energy gap decrease with the increasing of the weight percentage of the added nano particles, this attributed to the creation of on site levels in the energy gap,the transition in this case is conducted in two stages that involve the transition of an electron from the valence band to the local levels as a result of increasing Ag percentage. This behavior is attributed to the fact that composites are of heterogeneous type (i.e.the electronic conduction depends on added Ag nanoparticles), the increase of the added rate provides electronic paths in the polymer which facilitate the crossing of electrons from the valence band to the conduction band,this explains the decrease of energy gap with the increase of the concentration of the additive [12]. The forbidden transition of the indirect energy gap is

calculated in the same way.

Figure 9 shows the forbidden transition of the indirect energy gap for the (PMMA-Ag) composites.

Atomic force microscope (AFM)

Figure(10,11,12,13,14,15) shows AFM images of samples in two and three dimensions. All the images show homogeneous distribution with columnar structure.

The average diameters, root mean square (RMS) and the average roughness of the films are Listed in TABLE 2. It was observed that the diameter of all samples is about the range of nanoscale. Also, it was shown very smooth surface with small roughness, smoothing of the films is possibly due to order of surface atoms to attain a lower energy state.
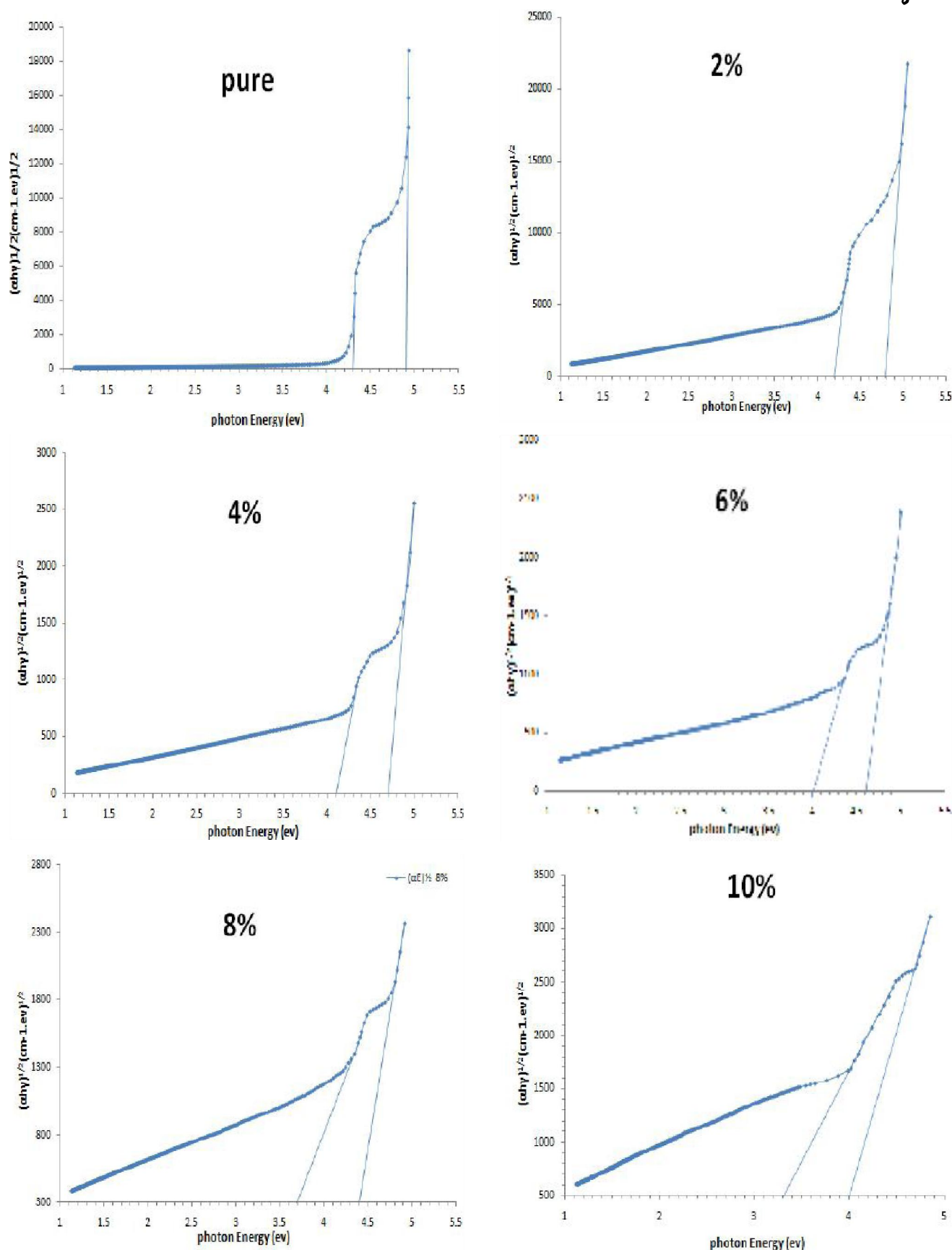
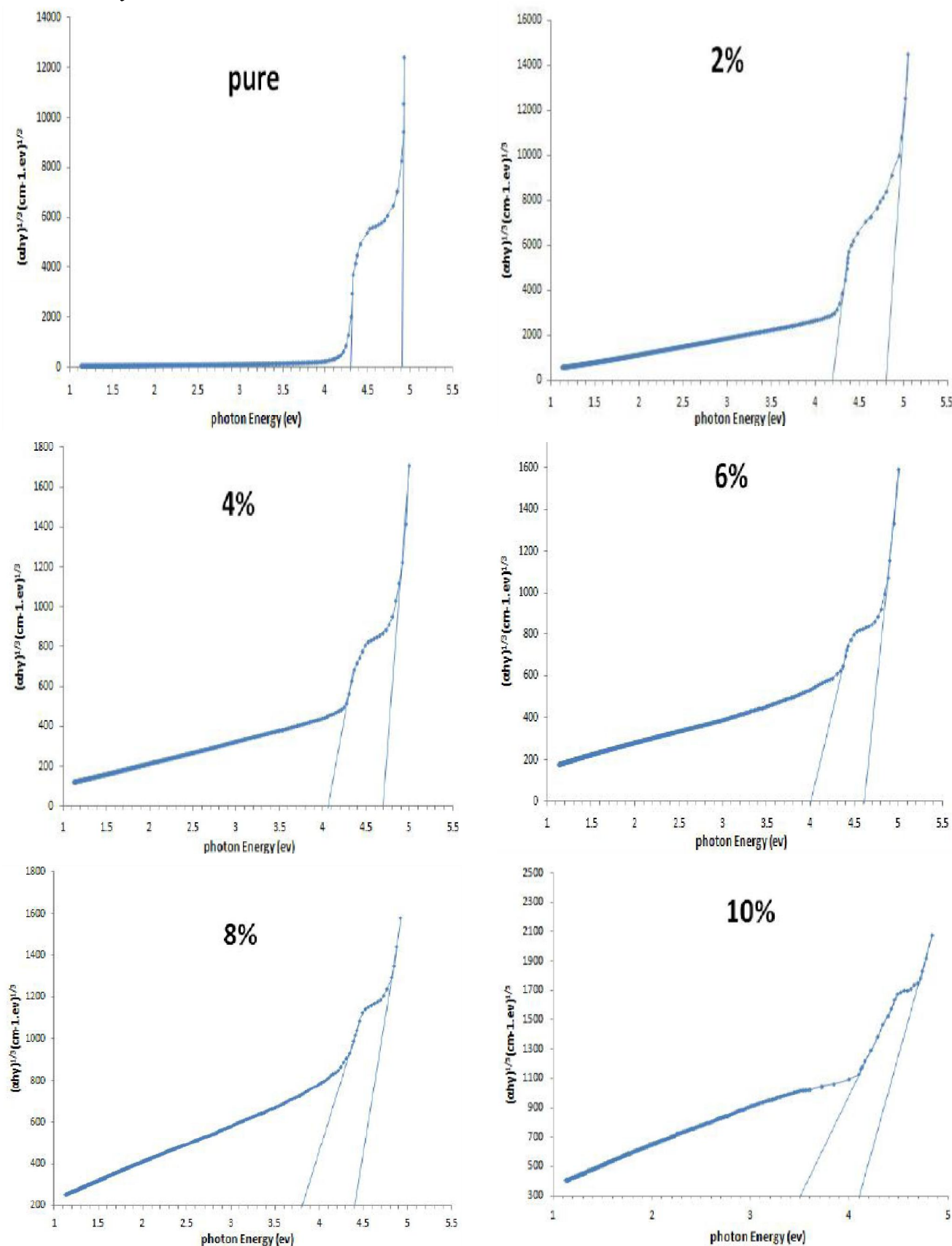**Figure 8 : The energy gap for the allowed indirect transition as a function of photon energy of (PMMA-Ag) composites**

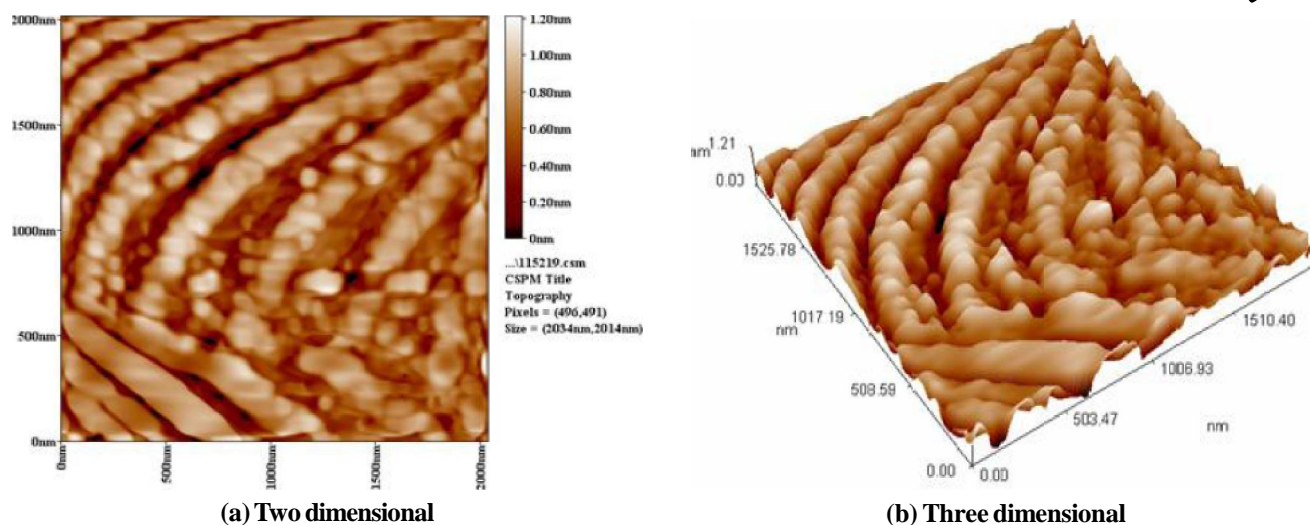**Figure 9 : The energy gap for the forbidden indirect transition as a function of photon energy of (PMMA-Ag) composites**
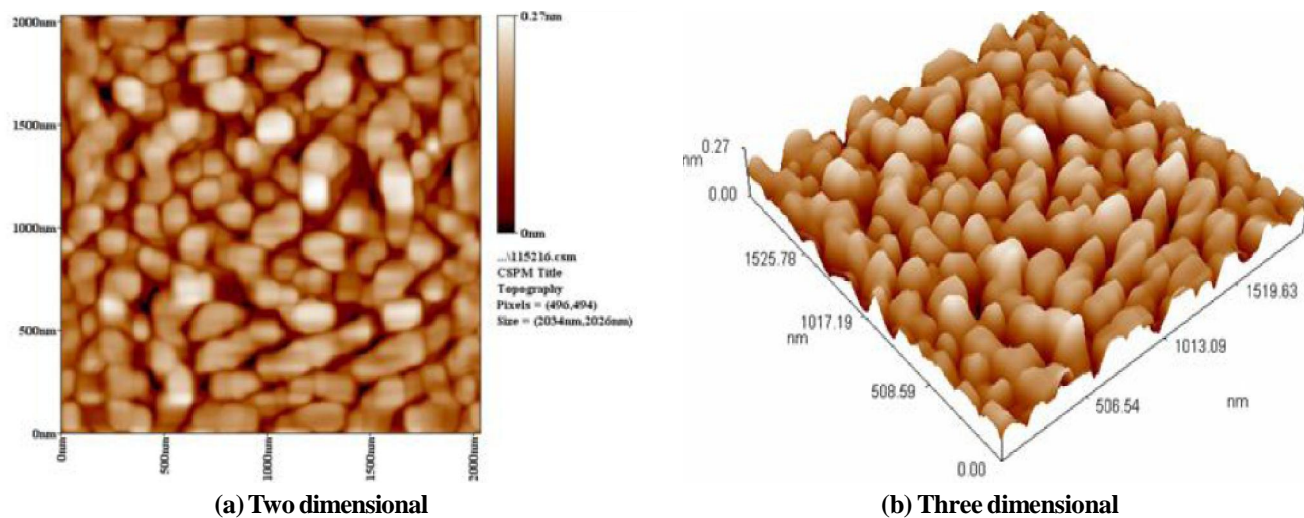
(a) Two dimensional   (b) Three dimensional

Figure 10 : AFM images for sample pure

(a) Two dimensional   (b) Three dimensional

Figure 11 : AFM images for sample 2%

(a) Two dimensional   (b) Three dimensional
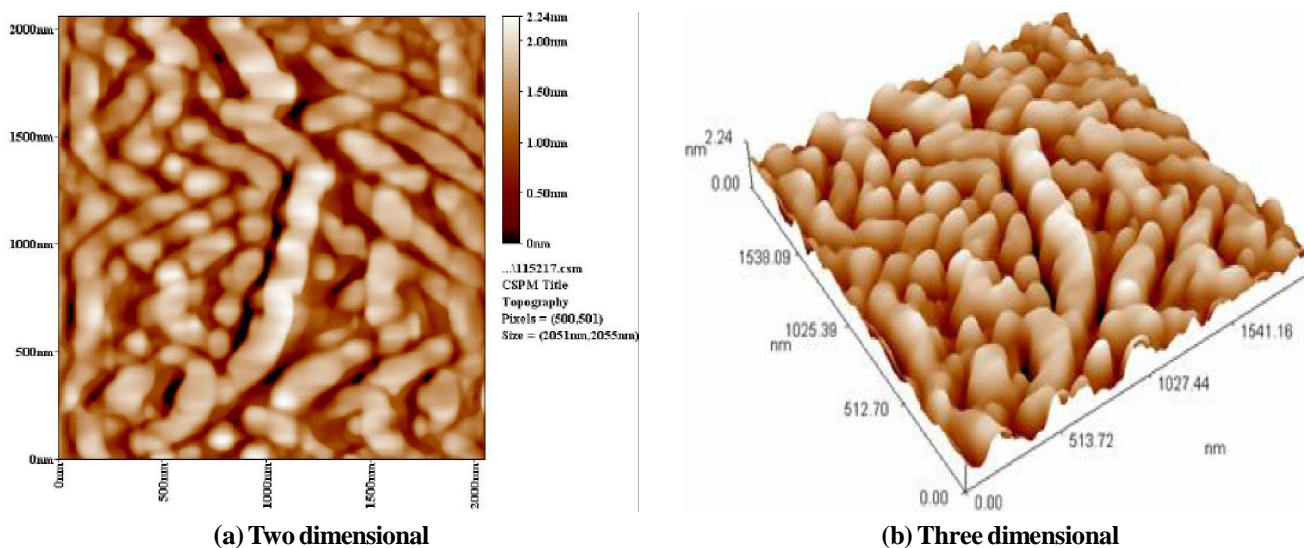
Figure 12 : AFM images for sample 4%

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(a) Two dimensional   (b) Three dimensional
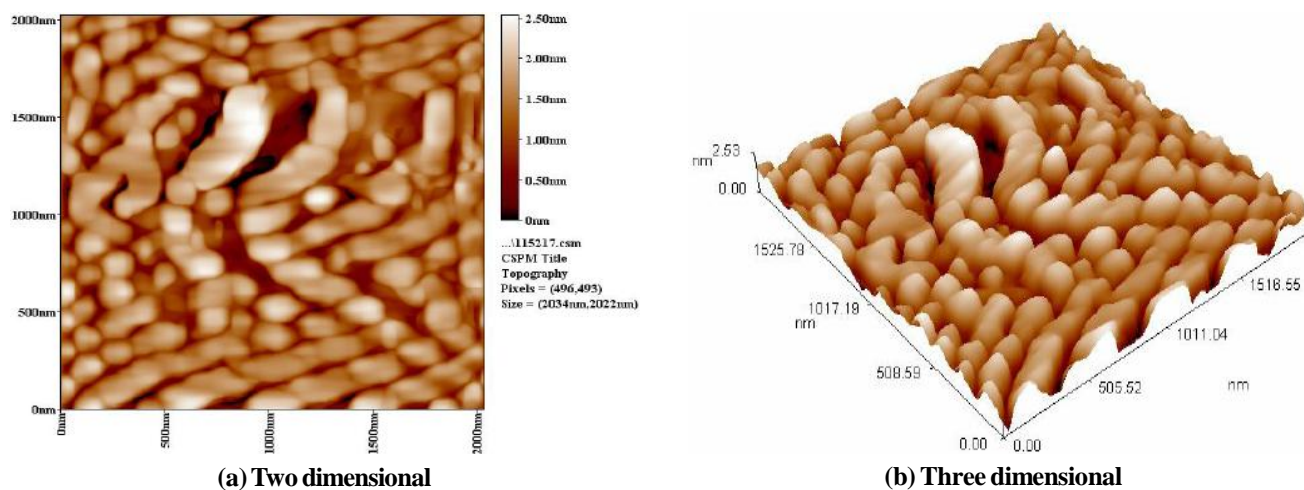
Figure 13 : AFM images for sample 6%

(a) Two dimensional   (b) Three dimensional

Figure 14 : AFM images for sample 8%

(a) Two dimensional   (b) Three dimensional
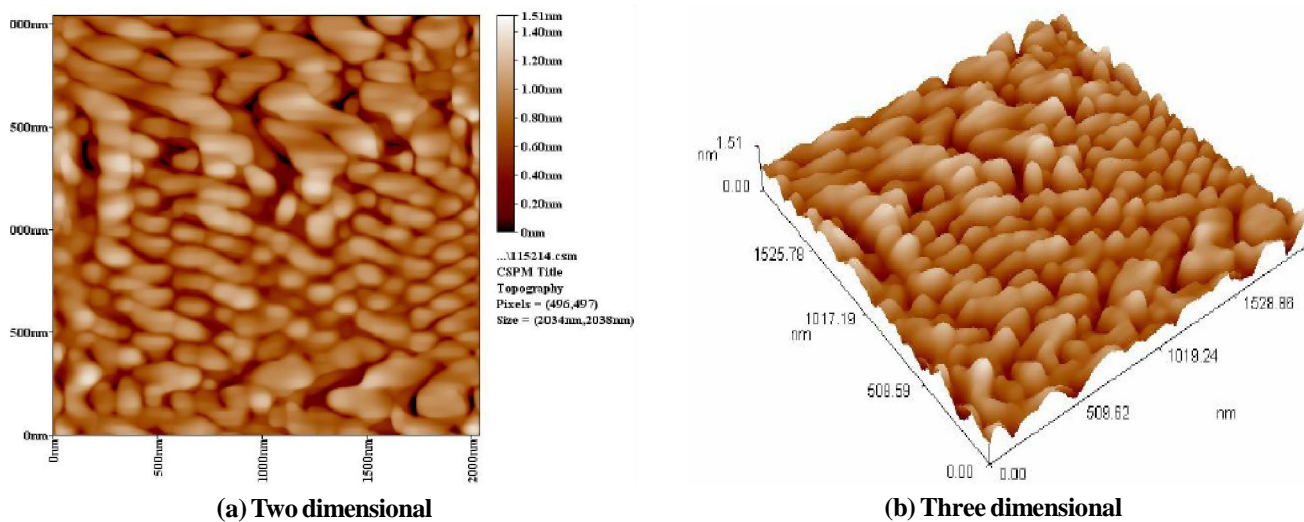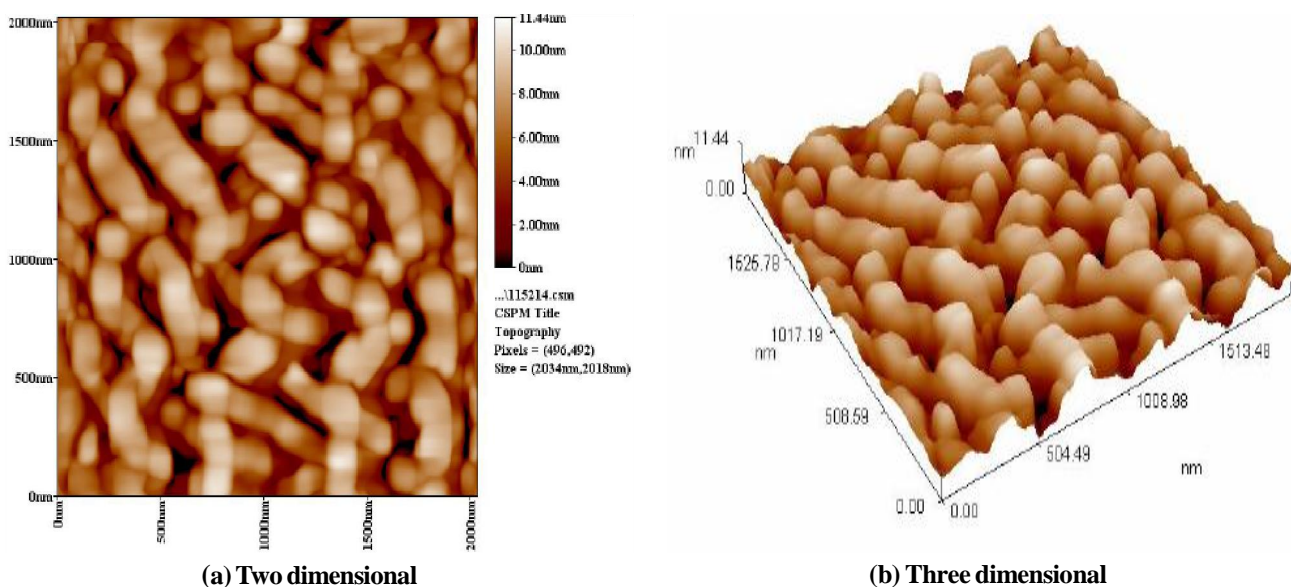
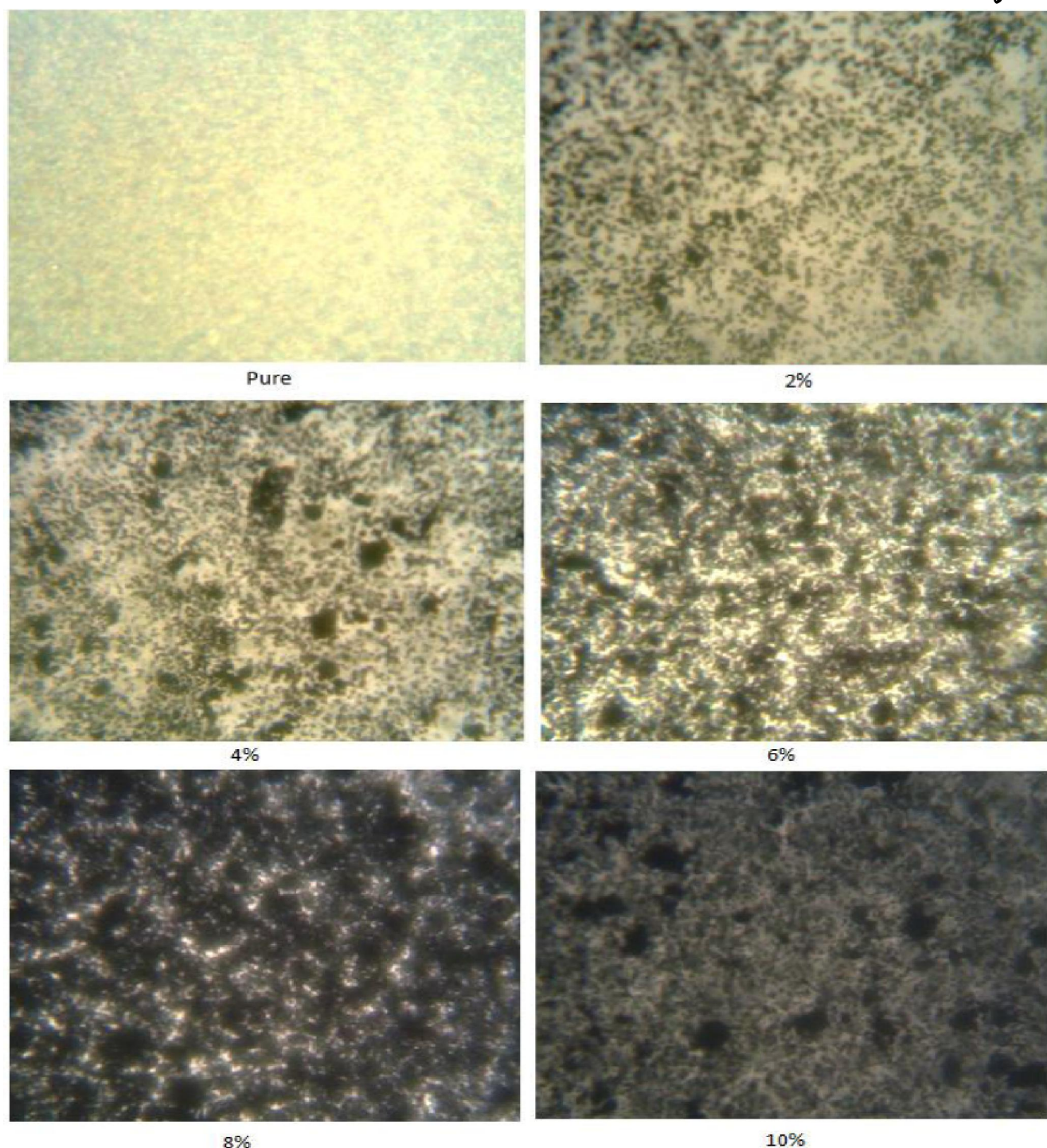**Figure 15 : AFM images for sample 10%**

Figure 16 : Photo micrographspower (X 400)

The optical microscope

The following Figure 16 shows the optical micrograph of (PMMA-Ag) nanocomposite.

The first film (pure PMMA) tends to white color, this is a color of the polymer (PMMA) then increase the proportion of Ag (2%, 4%, 6%, 8% and10%) the color of films tends to be dark (nearly black) which reflect the metallic nature of Ag, then it look dark black at 10%.

CONCLUSIONS

1 The Electronic Transitions are indirect transitions.

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2   Optical energy gap decreases with increasing of Ag nanoparticles concentration.

3   The result of Optical Microscope show homogeneous distribution from (PMMA-Ag).

4   The result of Atomic Force Microscope show very smooth surface and small roughness.

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