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Preparation of Composite Polymethylmethacrylate /Silver (PMMA/Ag) Films and Studying the Effect of Silver Nanoparticles on their Optical Properties

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Abstract:

In this work to a realization the effect of nanoparticle of Silver on the optical properties of Polymethylmethacrylate (PMMA) films prepared by using casting technique at a temperature (50°C) with thickness (8±1μm). The optical properties of the composite were done by measuring the absorption and transmission spectra as a function of wavelength (200-800) nm. The results of measurement showed that the transmittance of the films decreased with increasing the addition of silver nanoparticle due to increasing of attenuation of incident light with a clear increase of absorption and a decrease in optical reflectivity. As well as calculated the optical constants (α,k, and εr) of the prepared films and the results showed an increase when increasing addition.The real part (εr) of the dielectric constant behave like the refractive index, while the imaginary part (□i) of the dielectric constant behave like the extinction coefficient, as for optical conductivity its values increases as increasing the rate of the Nano silver , and the identifying of the types of electronic transitions and determining energy gaps. It was found there is diminution in energy gap for direct electron transmission reaching values (5.4 - 4.9) eV.

Keywords: *Polymethylacrelate, Composite materials , Optical Properties, Silver Nanoparticle.*

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I. INTRODUCTION

Polymethylmethacrylate (PMMA) has a wide variety of uses and is employed in many applications where strength and durability are needed such as medicine bone cement dentistry dentures, and as a low-cost replacement for glass "Plexiglas".It is also distinguished by having distinctive transparent properties due to the colorlessness and the ability to pass light at a rate of sometimes up to 92%, and therefore it is widely used in transparencies as well as in some distinctive applications in lenses [1,2]. Polymers it consists of repeating units of monomers that have distinct applications in daily life PMMA with a glass transition temperature of ~100°C. Because of the wide variety of applications used in different environments, PMMA has become an important topic for many studies focusing on solving to problems related to improving properties such as strength and durability. [3,4]. To improve the characteristics of the industrial polymer, selected substances with certain properties are added. Additives and Auxiliaries are applied to The polymer either in a physical or dissolved form in the polymer solution or as surface layers so as not to affect the chemical composition of the polymer but affect the physical properties by influencing the shape and Composition of molecules, If one or more

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chemicals are added to the polymer, such as a simple or complex metal or salt, etc., to obtain the desired qualities, the mixture (polymer + additives) is called the (polymer system)[5,6]. To improve optical properties to Polymethylmethacrylate (PMMA) films silver nitrate ($AgNO_3$) was added at different volume rates (3, 6 and 9)%.

II. Materials and Methods

The PMMA solution is prepared by dissolving a (1g/ml) of PMMA powder in affixed volume (100 mL) of Dimethylformamide (DMF), and dissolving (0.849g/ml) of silver nitrate $AgNO_3$ its molar concentration solution (0.1) was determined by the following equation [7]:

$$C_m = \frac{m}{V} \times \frac{1}{Mw} \quad \text{.................} \quad (1)$$

Where (*m*) represents the mass of the solute and (*V*) is the volume of the solution (solvent) and (M_W) represents the molecular weight. in (100mL) of distilled water by using magnetic stirrer for 10 a minuteto ensure the melting of the material were mixed at 50°C. To obtained a homogenous solution , it is appropriate mixing PMMA with different weight percentage of $AgNO_3$ (3 , 6, 9) % , after which solution was transferred Method of casting to glass Petri dish of (7cm) in diameter placed on a from a flat panel for a period of (7 days). The dried and prepared film is easily raised using forceps. the measure the thickness of the samples by used digital vernet to be (8±1µm).

Results and Discussion

The optical properties of all sample were during the measurement of the transmittance spectrum within the wavelength range (200-800 nm) were measured at room temperature, by using UV-VIS spectrophotometer(SCINCO-MEGA-2100 Range 0 MEGA-2100):

1: Optical Absorbance

The optical properties of nanoparticles are highly dependent on size changes in composition, and the influence of size on the optical absorption spectrum of metallic nanocrystals is the best known to identify noble metallic nanoparticles such as gold and silver [9]. In Fig.1 optical spectra of silver – polymer PMMA:Ag nanocomposites revealed the presence of the silver nanoparticle surface Plasmon [10]. The nanocomposites produced by variation of silver a concentration of were shown shifting the Plasmon resonance wavelength in the UV-VIS region .the surface plasmon resonance (SPR) absorption peak With a concentration of 3% shifts to the longer waves (300-up to 600 nm) with a concentration of 9%, with the band broadening significantly. host (Ag) enhances the absorbance of the composite films [11,12].

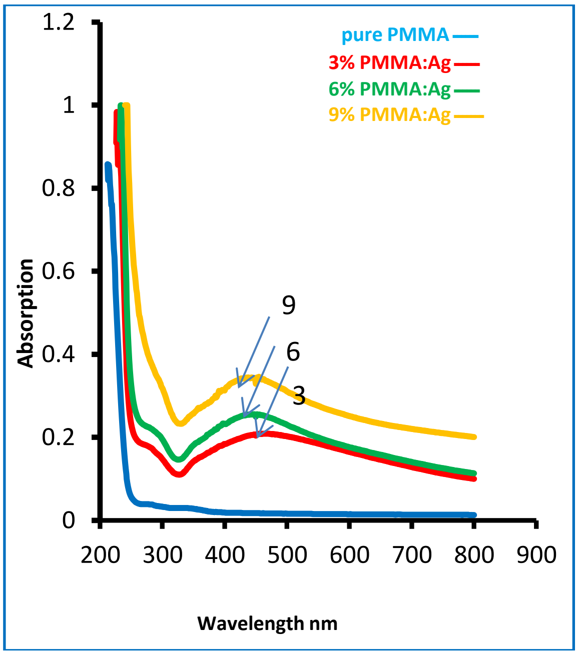

Fig. (1) Absorption spectra of (PMMA,PMMA:Ag).

2: Optical Transmittance

In Fig. 2 shows the spectral transmittance to the range of wavelengths from (200-800 nm) for before and after adding Ag ,(PMMA),(PMMA:Ag)It was obvious that it conduct was opposite to that of the absorption, This behavior is attributed to increased interaction of the light beam after the addition of Ag, so any increase in absorbance values cause decrease in the values of transmittance [13].

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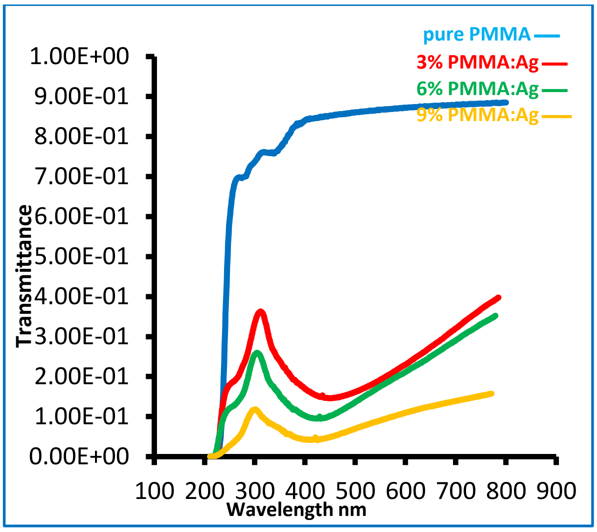

Fig.(2) Optical transmittance spectra of (PMMA,PMMA:Ag).

3:Optical Reflection

The value of the optical reflection can be calculated and estimated by the absorbance and transmission spectrum values according to the energy conservation law, and from the following relationship [14] :

R+T+A=1…...……….(2)

Fig.3 shows that the reflectivity values increase with increasing concentration, which means an increase in the number of Silver particles, Thus increasing the density, this means that the reflectivity depends entirely on the density of the material .

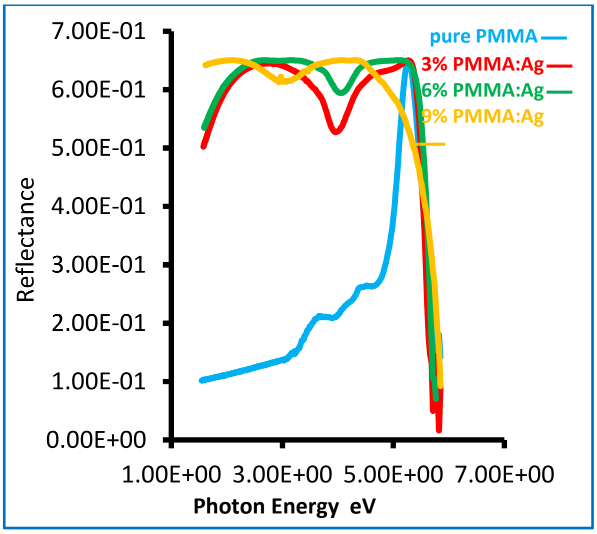

Fig. (3) Optical reflection spectra of (PMMA,PMMA,Ag).

4: Optical Conductivity

Fig.4 explicates Optical conductivity , it is refer to increase of the number of charge carriers (electrons or gaps) result from the fall of a light beam on the material.From the figure , it is clear that the values of the optical conductivity were increased with increasing of photon energy and the addition of the number of Silver particles. Optical conductivity can be calculated using the relation [15]:

$$\sigma_{opt} = \frac{\alpha\, n\, c}{4\,\pi} \quad \ldots\ldots\ldots\ldots\ldots(3)$$

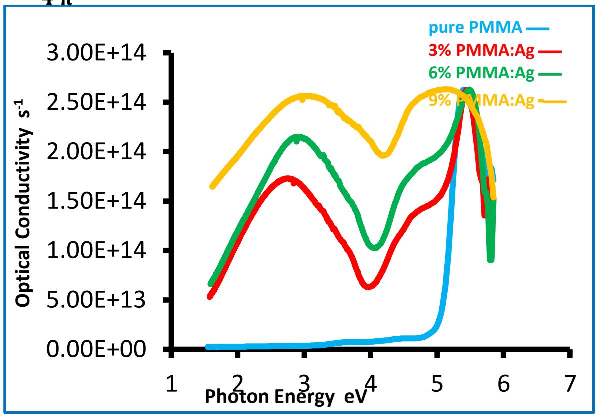

Fig. (4) Optical Conductivity spectra of (PMMA,PMMA,Ag).

5:Absorption Coefficient

The absorption coefficient (α) represents the ability of a substance to absorb light at a given wavelength (λ) and has been calculated using the relationship [16] :

$$\alpha = \frac{2.303\ A}{t} \quad \ldots\ldots\ldots\ldots\ldots(4)$$

Where A represent the substance absorption and t is the thickness of the sample in cm.

Fig.5 explicates increment of absorption coefficient values with an increment of addition concentrations from Ag,

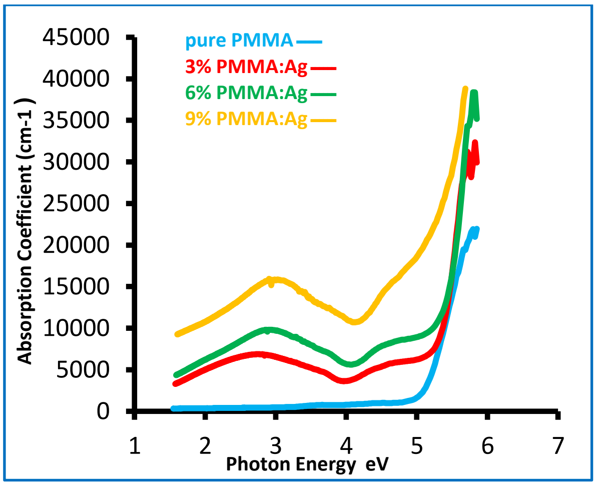

Fig.(5) Absorption coefficient spectra of (PMMA,PMMA:Ag).

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that led to the increase of light absorbed because the interaction of the electromagnetic wave and the molecules increases with concentration, according to the law of Lambert- Bear (4)and thus increase the absorption coefficient.

6: The Extinction Coefficient

The extinction coefficient(K_o) represent the amount of energy absorbed, was calculated using the relation **[17]:**

$$K^o = \frac{\lambda\alpha}{4\pi} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

The change of the extinction coefficient as a function of the wavelength can be seen in Fig.5 for (PMMA-PMMA:Ag). It can be noted that (k) increases with the increase of the concentration of (Ag) nanoparticles. the reason for this to increased absorption coefficient with the increase of weight percentages of (Ag) nanoparticles,the increases in (k) was due to the optical energy gap decreasing until it reached the value (4.9 eV). the behavior of (k) was nearly comparable and like to corresponding absorption coefficient in fig.6.

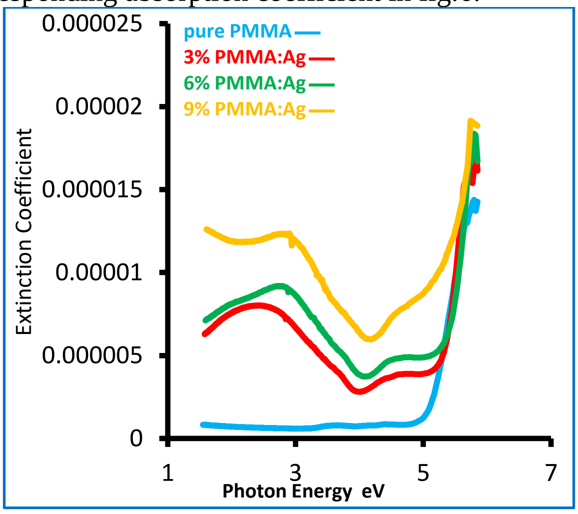

Fig. (6) Extinction coefficient spectra of (PMMA,PMMA:Ag).

6: The Refractive index

refraction index (n) of a material is the ratio of the velocity of the light in a vacuum to its velocity through a medium, the refractive index is calculated from following equation [17]:

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Fig.7 showed the variation of refractive index as a function of wavelength for the (PMMA) films , before adding and after adding concentration (3,6,9)% of (Ag) nanoparticles. It was found that refractive index was decreasing with increasing adding (Ag) nanoparticles, with increasing photon energy eV. [18]

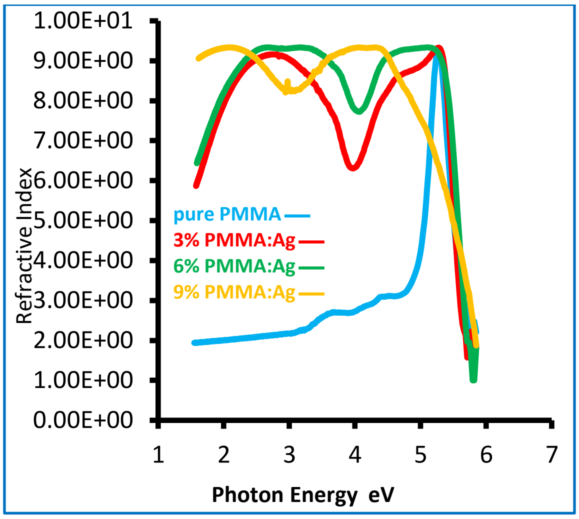

Fig. (7) Refractive index as a function of photon energy of (PMMA,PMMA:Ag).

7:The Dielectric Constant

Dielectric constant is defined as the response rate of the substance toward the incident electromagnetic field, and divided into real (ε_r) and imaginary part(ε_i), and they can be calculated by :

$$\varepsilon_r = n^2 - k^2 \quad \ldots\ldots\ldots\ldots\ldots (7)$$

$$\varepsilon_i = 2nk \quad \ldots\ldots\ldots\ldots\ldots (8)$$

$$\varepsilon = \varepsilon_r + i\varepsilon_i \quad \ldots\ldots\ldots\ldots\ldots (9)$$

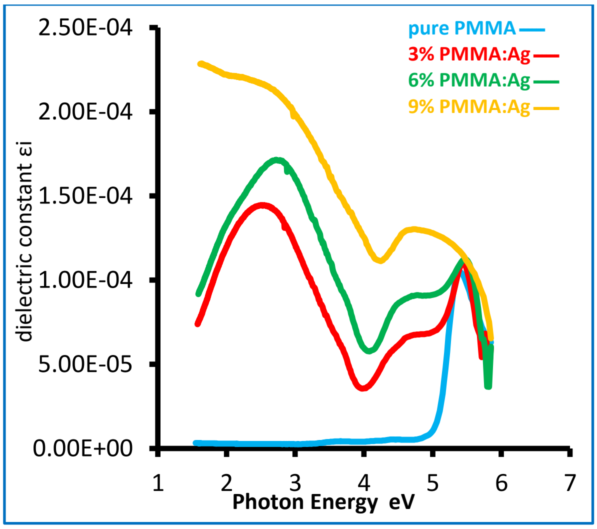

Fig.(8) Imaginarypart (ε_i) as a function of photon energy of (PMMA,PMMA:Ag).

The real (ε_r) and imaginary part (ε_i) of (PMMA, PMMA:Ag), befor and after adding concentration (3,6% and 9%) of (Ag) nanoparticles. It is illustrated in Figs. 8, 9 respectively. these results shows (ε_r) for all samples behaves as refractive index because of the smaller value of k^2 comparison with n^2, while the imaginary part

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behaves as the extinction coefficient, because it's depend on
k-values[16,17].

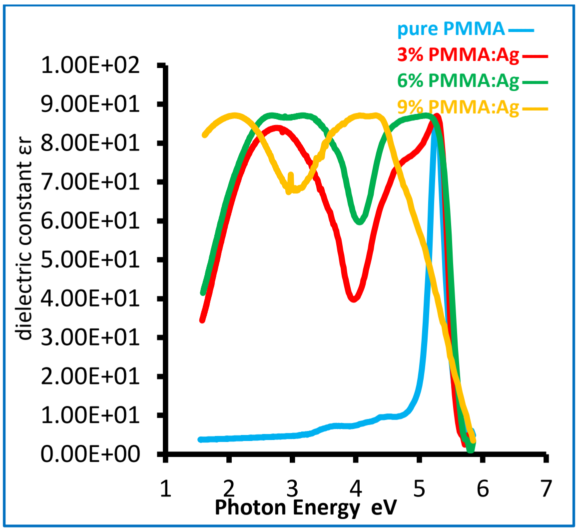

Fig.(9) Real part (ε_r) as function of the wavelength for (PMMA,PMMA:Ag).

8:The Opticalenergy gap (Eg)

The energy gap (Eg) can be calculated using the (Tauc) model, was obtained by (αhν) 1/r, versus (hν) with (r) values equal to (1/2, 2, 3/2). the best fitted with (r = 2), which indicates to a direct transition [7],[19]. Fig.10 shows while increasing the (Ag) concentration the energy gap showed a decrescent in values, for the forbidden direct transition of (PMMA,PMMA:Ag), is due to for the creation of local levels in the forbidden optical energy gap, the increase of the silver nanoparticles provides electronic paths inside the polymer which simplify the transit of an electron from the valence to the conduction band.

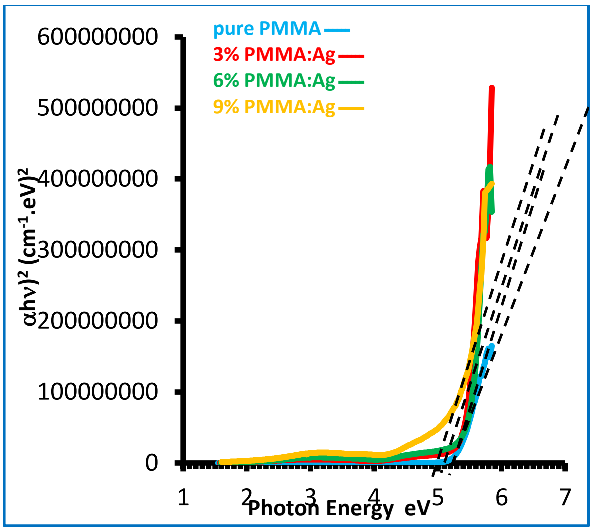

Fig.(10) The energy gap values of the direct transition forbidden for (PMMA,PMMA:Ag).

CONCLUSIONS

The concentration of Ag nanoparticles has strongly affected on optical properties of (PMMA,PMMA:Ag) As shown by the results It was found there is an increase in the absorption and optical conductivity with the increasing the doping concentration of silver nanoparticles with ratios (3,6,9)%. the result of concentration of silver nanoparticles have shown an increasing in an optical constants(α,k,ε_i) due to doping process. the increasing of (Ag) concentration showed decrescent in values for energy gap for the forbidden direct transition for (PMMA, PMMA: Ag) and with these results the polymer films can be utilized in medical and an electronic applications.

Table.1.The parameters of optical properties for(PMMA,PMMA:Ag) films.

Additive Concentration Ag%	T	σ $_{opt}s^{-1}$	α (cm^{-1})	N	K	εr	εi	Eg (eV)
	λ:250 (nm)	λ:256 (nm)	λ:250 (nm)	λ:245 (nm)	λ:250 (nm)	λ:256 (nm)	λ:245 (nm)	
0% PMMA	0.59	1.04×10^{13}	163.2	5.0×10^{2}	1.11×10^{-6}	6.15×10^{-6}	2.52×10^{1}	5.4
3% PMMA:Ag	0.11	1.65×10^{14}	892.2	8.7×10^{2}	4.56×10^{-6}	7.33×10^{-5}	0.70×10^{1}	5.3
6% PMMA:Ag	0.04	2.23×10^{14}	1253	6.4×10^{2}	6.41×10^{-6}	9.92×10^{-5}	4.21×10^{1}	5.2
9% PMMA:Ag	0.001	2.40×10^{14}	2716	1.8×10^{2}	1.38×10^{-5}	1.07×10^{-4}	3.51×10^{2}	4.9

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