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RESEARCH ARTICLE

Effect of Addition of Silver Nanoparticle on Optical Properties of Polymethylacrelate (PMMA) Films

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Abstract

The aim of this work to a realization the effect of adding silver nanoparticles on the optical properties of Polymethylmethacrylate (PMMA) films were prepared by using casting technique At a temperature (50°C) with thickness (8±1µm). The optical properties by measuring the spectra absorbability and transmission as a function of wavelength (200-800) nm. The results showed that the transmittance decreased with increasing doping because of increased impurity resulted holds attenuation in the intensity 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 ϵ r) of the prepared films and the results showed an increase when increasing rate of doping the real part of the Dielectric Constant conduct like the refractive index, while the imaginary part conduct like the extinction coefficient, as for optical conductivity its values increases with increasing the rate of the silver nanoparticles as well as identifying the types of electronic transitions and calculating energy gaps It was found there is diminution in energy gap for direct electron transmission reaching values (5.4 - 4.9) eV.

Keywords: Polymethylacrelate, Optical Properties, Silver Nanoparticle, Optical Conductivity.

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 also as a low-cost replacement for glass "Plexiglas", It has the best transparency and optical properties It is colorless with a 92% light transmission, It comes in a full range of transparencies. some of its applications are lenses[1, 2]. Polymers are comprised of repeating structural segments and are found in a wide variety of everyday products. PMMA with a glass transition temperature of ~100°C.

Due to its diverse range of applications and potential end-use environments, PMMA has been the subject of numerous studies focusing on the improvement of 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 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 (AgNO₃) was added at different volume rates (3, 6 and 9) %.

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 AgNO₃ its molar concentration solution (0.1) was calculated through the following equation [7]:

$$C_{\rm m} = \frac{m}{V} \times \frac{1}{MW} \dots (1)$$

Where: m is the mass of solute, V is the volume of solution, and Mw is the molecular weight.

In (100mL) of distilled water by using magnetic stirrer for 10 a minute to ensure the melting of the material were mixed at 50°C. Then mixing PMMA concentrate [8] on with different weights percentage of AgNO₃ (3,6, and 9)% a homogenous solution was obtained. after which solution 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 film was then removed easily by using a tweezer. The measure the thickness of the samples by used digital vernier to be $(8\pm1\mu m)$.

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

recorded at room temperature, by using UV-VIS spectrophotometer(SCINCO-MEGA-2100 Range 0 MEGA-2100):

Optical Absorbance

Optical properties of nanoparticles are closely related to size-dependent changes in the structure. Size influence on the optical absorption spectra of metallic nanocrystals is best known for the noble metal nanoparticles such as gold and silver [9]. In Fig.1 optical spectra of silver-polymer PMMA: 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 (300-up to 600 nm) with concentration of 9%. with the broadening significantly. host (Ag) enhances the absorbance of the composite films [11,12].

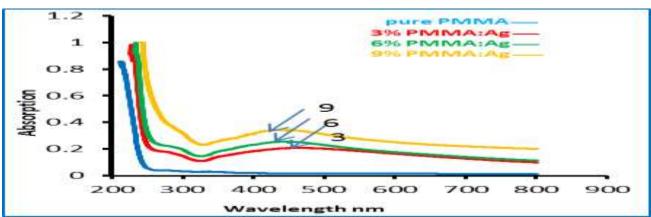


Fig.1: Absorption spectroscopy of (PMMA, PMMA: Ag)

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].

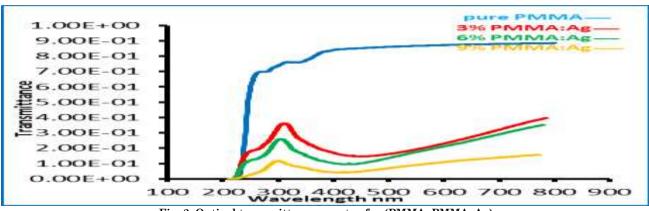


Fig. 2: Optical transmittance spectra for (PMMA, PMMA: Ag)

Optical Reflection

Optical reflectance can be achieved from absorption and transmission spectra in

accordance with the law of preservation of energy by the following relation [14]:

Fig.3 shows that reflectance values increase with increasing concentration as a result of increase the number of Silver particles

therefore increase the density, whereas reflectivity is completely dependent on the density for material.

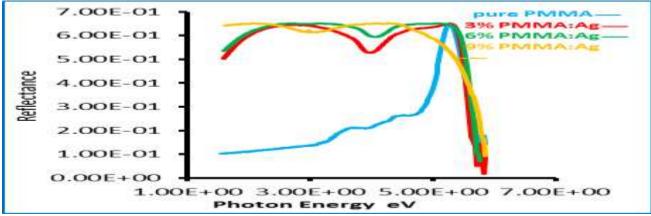


Fig. 3 Optical reflection spectra of (PMMA, PMMA, Ag)

Optical Conductivity

Fig.4 explicates Optical conductivity is the increase in the number of charge carriers (electrons or gaps) due to the fall of a light beam on the material.

We observe an increase in optical conductivity values with increasing photon energy and increasing the addition of silver particles, Optical conductivity can be calculated by the following equation [15]:

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

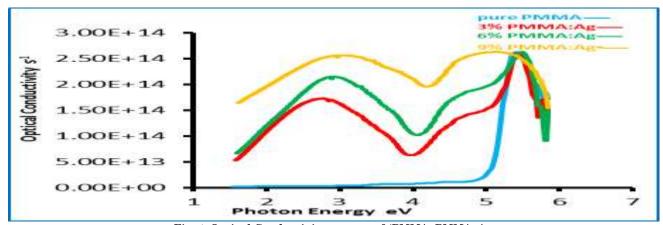


Fig. 4: Optical Conductivity spectra of (PMMA, PMMA, Ag

Absorption Coefficient

Absorption coefficient (α) is defined as the ableness of a material to absorb the light of a

given wavelength (λ), was calculated by the following equation [16]:

$$\alpha = \frac{2.303 \text{ A}}{t} \dots (4)$$

Where: A is the absorption of the substance, t: the sample thickness in cm.

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

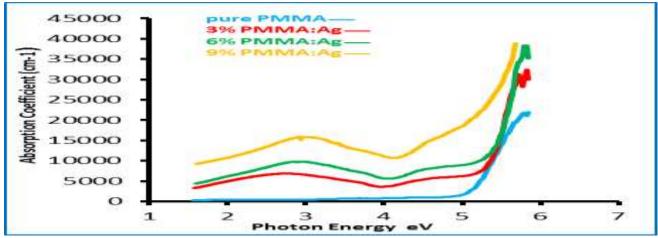


Fig.5: Absorption coefficient versus wavelength for (PMMA, PMMA: Ag)

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 increases the absorption coefficient.

The Extinction Coefficient

The extinction coefficient (K₀) is defined as the amount of energy absorbed, was calculated by the following equation [17]:

$$\mathbf{K}^{\scriptscriptstyle 0} = \frac{\lambda \alpha}{4\pi} \dots (5)$$

The change of the extinction coefficient as a function of the wavelength is shown 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 behaviors of (k) were nearly comparable and like to corresponding absorption coefficient in Fig.6.

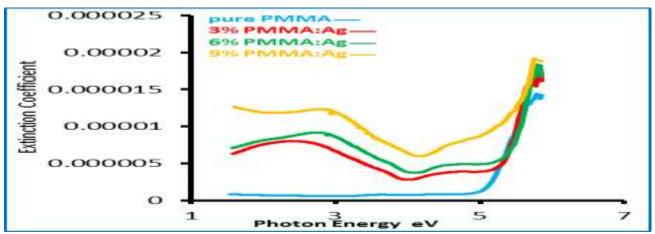


Fig.6: The extinction coefficient as a function to wavelength for (PMMA, PMMA: Ag)

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]:

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}}$$
(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].

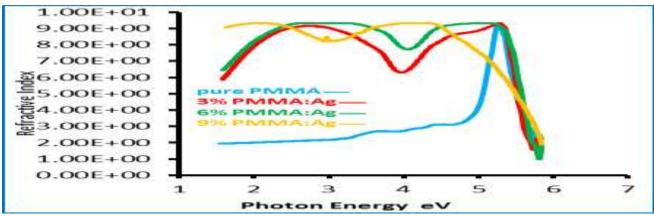


Fig.7: The refractive index as a function to wavelength for (PMMA, PMMA: Ag)

The Dielectric Constant

Dielectric constant is defined as the response rate of the substance toward the incident electromagnetic field, the dielectric constant divided into parts real (\Box r) and imaginary (\Box i), the real and imaginary parts of dielectric constant (\Box r and \Box i) can be calculated by using equations:

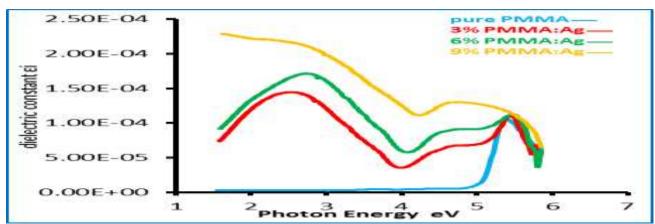


Fig.8: The imaginary part (ci) of the dielectric constant as a function of the wavelength for (PMMA, PMMA: Ag)

The real part (er) and imaginary part (ei) of (PMMA, PMMA: Ag), before adding and after adding concentration (3, 6 and 9) % of (Ag) nanoparticles. It is illustrated in Figs.8.9 to respectively. These results show that in all samples the real part behaves such as the

refractive index, while the imaginary part behaves such as the extinction coefficient, the behavior of ϵr is similar to refractive index because of the smaller value of k^2 comparison of n^2 , while ϵr imaginary Based on values the k-value [16, 17].

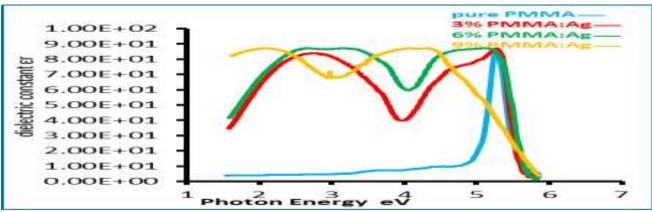


Fig.9: The real part (er) of the dielectric constant as a function of the wavelength for (PMMA, PMMA: Ag)

The Optical Energy Gap (Eg)

The energy gap (Eg) can be calculated using the (Tauc) model, was obtained by (αhv) 1/r, versus (hv) with (r) values equal to (1/2, 2, 3/2). The linear portion was best fitted with (r = 2), which indicates a transition of direct type [7, 19]. Fig.10 shows decreasing energy gaps with the increase of the concentration of the Ag nanoparticles, for the forbidden direct transition for (PMMA, PMMA: Ag), this is due to the reason for the creation of local

levels in the forbidden optical 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 to the conduction band result of increasing the concentration silver nanoparticles. The increase of the silver nanoparticles provides electronic paths in the polymer which facilitates the crossing of an electron from the valence band to the conduction band.

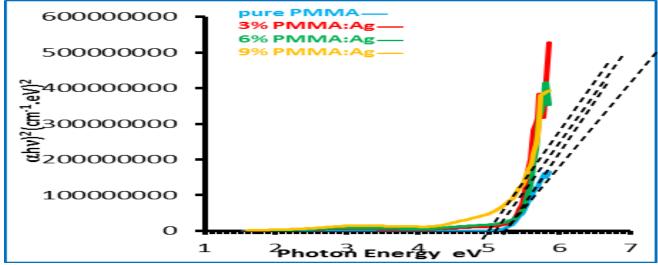


Fig. 10: The energy gap values of the direct transition forbidden for (PMMA, PMMA: Ag)

Conclusions

That the concentration of Ag nanoparticles has strongly influenced the 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 of the doping concentration of silver nanoparticles with ratios used (3,6,9)%.

It was seen there is the increase in optical constants (a, k, ɛi) for increase doping of concentration of silver nanoparticles. It happened decreasing energy gaps with the increase of the concentration of the Ag nanoparticles, for the forbidden direct transition for (PMMA, PMMA: Ag) with these results the polymer films can be utilized in medical and electronic applications.

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

| Additive | Т | | a (cm ⁻¹) | N | K | $\Box \mathbf{r}$ | □i | Eg |
|---------------|-------|-----------------------|-----------------------|---------------------|-----------------------|-----------------------|----------------------|------|
| Concentration | | o opt S⁻¹ | | | | | | (eV) |
| Ag % | λ:250 | λ:256 (nm) | λ:250 | λ:245 | λ:250 (nm) | λ:256 (nm) | λ:245 (nm) | |
| | (nm) | | (nm) | (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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