

To Study the Silver Concentration Effect on the Optical and Electrical Properties of the Ag/PMMA Composites

Dr.Nahida G.Hamed

Applied Physes department, School of Applaid science, University of Technology/Bagdad

Email:dramashadani@yahoo.com

Maraw Rahem

Ministry of Science, University of Technology/Bagdad

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ABSTRACT

The present work was carried out to investigate the silver concentration Effect (Ag %) othe optical and the electrical properties of the polymethyl methacrylate (PMMA). The samples were casted as films from the photopolymer (PMMA) stated above and the reason. The optical constant (α, k, n, ϵ_r , and ϵ_i) for the photopolymer (PMMA), and Ag/PMMA composites at different concentration were investigated. It was seen that there was nonlinear relationship between the optical constants and the concentration ratio, which was attributed to their incompatibility. These results were confirmed with optical micrographs. It was found that there was increasing of carrier concentration with Ag ratio which Ag/PMMA composites at different concentration. These prepared polymer systems were analyzes spectrophotometrically. It was found that an increasing in the absorption spectra with increasing of the silver concentration in Ag/PMMA composites, which was attributed to the increasing in localized states. The results proved that its energy gap was for 13% Ag/PMMA (4.85eV), which was the lowest of all polymer system involved due to previous was caused decreasing in the mobility. The results showed that the best conductivity was at 9% Ag ratio, and the lowest receptivity.

Key words: Ag/PMMA, Electrical, Optical Constants.

دراسة تأثير تركيز الفضة على الخواص البصرية والكهربائية لمترابك AS/PMMA

الخلاصة

اجري البحث لدراسة تأثير تركيز الفضة (Ag%) على الخواص البصرية والكهربائية للبولي مثيل ميثااكرليت (PMMA). صببت النماذج على شكل اغشية رقيقة من البوليمر النقي (PMMA) ومترابكات (Ag/PMMA) وبترابك مختلفة. حللت النماذج طيفاً لقد وجد ازدياد اطياف الامتصاصية بازدياد تركيز الفضة في المترابكات (Ag/PMMA), وقد اعزى ذلك الى ازدياد المستويات الموضوعية. اظهرت النتائج بان فجوة الطاقة للمترابك (13% Ag/PMMA) كانت (4.85ev), والتي

تمثل اقل فجوة طاقة لجميع المنظومات البوليمرية مدار البحث للاسباب السابقة الذكر. لقد تم دراسة الثوابت البصرية (α, k, n, ϵ_r and ϵ_i) للبوليمر (PMMA) ومترابكات (Ag/PMMA) وبتراكيز مختلفة. وجد علاقة غير خطية بين تراكيز الفضة والثوابت البصرية ويعود ذلك الى عدم تمام التوافق ما بين الفضة والبولي مثيل ميثاكرليت. لقد عززت النتائج بالصور الفوتوغرافية. وجد ازدياد في تركيز حاملات الشحنة بازدياد تركيز الفضة (Ag%) والذي يؤدي الى تناقص في الحركية. اظهرت النتائج بان افضل توصيلة كانت للتركيز (9%Ag) وتناقص في المقاومة.

INTRODUCTION

The matrix is polymer, a polymer is a molecule made up of smaller molecules that are joined together by chemical bonds. The word polymer means many parts or units [1]. Polymer composites also can provide the greatest strength-to-weight and stiffness-to-weight ratios available in any material, even the lightest, and strongest metals [2]. Embedded in the other material called the matrix phase [3].

One of the goals of material research is to create new materials with Properties tailored to a particular application and to understand the optical and Electrical mechanisms that determine these properties.

One decade ago, the ion doped polymers were proposed as a new class of organic materials for real time holographic recording [4].

One of the newest methods to create such materials is doping of polymers with metals or salts, introduced into a polymer matrix, generally Improve the polymer behaviour and as a rule of composite materials, new Properties [5].

Polymer composites can be used in many different forms ranging from structural composites in the construction industry to the high technology composites of the aerospace and space satellite industries. Composites are combinations of two materials in which one of the materials, called the reinforcing phase, is in the form of particles, fibers.

Poly (methyl methacrylate) (PMMA) is an amorphous thermoplastic that can be delivered as clear as glass. The most widely used polymers in a variety of electronic applications where optical-grade materials are needed because of its excellent balanced properties paired with a reasonable PMMA has excellent clarity with high rigidity as a photopolymer [6].

The optical constants are very important because they describe the optical behavior of the materials. The absorption coefficient of the material is very strong function of photon energy and band gap energy [7].

Absorption is defined as the ratio between absorbed light intensity (I_A) by material and the incident intensity of light (I_0), Eq.

$$A = I_A / I_0 \quad \dots (1)$$

Transmittance (T) is given by reference to the intensity of the rays transmitting from the film (I) to the intensity of the rays incident on it (I_0) ($T=I/ I_0$), and can be calculated by [8]:

$$T = \exp [-2.303A] \quad \dots (2)$$

And Reflectance can be obtained from absorption and transmission spectra in accordance with the law of conservation of energy by the relation [8]:

$$R + T + A = 1 \quad \dots(3)$$

Absorption coefficient (α) is defined as the ability of a material to absorb the light of a given wavelength, Eq.(4)

$$\alpha = 2.303A/t \quad \dots (4)$$

Where A: is the absorption of the material and t is the sample thickness in cm. The Refractive index (n), the index of refraction of a material is the ratio of the velocity of the light in vacuum to that of the specimen [9-10].

$$R = ((n-1)^2 + k^2) / ((n+1)^2 + k^2) \quad \dots (5)$$

When $k \cong 0$

$$R = (n-1)^2 / (n+1)^2 \quad \dots (6)$$

$$n = (1+R^{1/2}) / (1-R^{1/2}) \quad \dots (7)$$

The extinction coefficient (k) was calculated using the following equation (Eq.8) [11].

$$K = \alpha\lambda / 4\pi \quad \dots (8)$$

Dielectric constant is defined as the response of the material toward the incident electromagnetic field. The dielectric constant of compound (ϵ) is divided into two parts real(ϵ_r), and imaginary (ϵ_i). The real and imaginary parts of dielectric constant (ϵ_r and ϵ_i) can be calculated by using Eq.8, Eq.10 and Eq.11. [10-11].

$$e = e_r - ie_i \quad \dots(9)$$

$$\epsilon_r = n^2 - k^2 \quad (\text{real part}) \quad \dots(10)$$

$$\epsilon_i = 2nk \quad (\text{imaginary part}) \quad \dots (11)$$

It is necessary to determine whether a material is n-type or p-type. Measurement of the conductivity of a specimen will not give this information but Hall Effect can be utilized to distinguish between the two types of carriers. Hall Effect is a phenomenon that occurs in a conductor carrying a current when the conductor is placed in a

magnetic field perpendicular to the current. The charge carriers in the conductor are reflected by the magnetic field, giving rise to an electric field (Hall field) that is perpendicular to both current (I) and the magnetic field (B) [12].

The Hall Effect is used to distinguish whether a semiconductor is n-type or p-type and to measure the majority carrier concentration and majority carrier mobility [13]. When the magnetic field (H=0.25 T) is applied perpendicular to the electric field, it yields a current (I) then the transverse (e.g.) which is called Hall voltage (V_H), is set up across the sample. So that the Hall coefficient (R_H) is given by [14].

$$R_H = \frac{V_H}{I} \times \frac{d}{H} \quad \dots (12)$$

Where d: is the thickness of the film.

The carrier density (n_H) is related to the Hall coefficient by the following equation:

$$n_H = \pm \frac{1}{qR_H} \quad \dots (13)$$

With the directions of control current and magnetic field illustrated, the charge carriers which produce the current are deflected to the front edge of the sample, therefore, the current is mainly due to electrons (as in the case of an n-type sample) the front edge becomes negatively charged. In the case of whole conduction (p-type sample) it becomes positively charged [15]. So from the sign of Hall coefficient (R_H) Eq. (12), we can determine the type of semiconductor that we have been used.

From (S) and (R_H) we may determine the Hall mobility.

$$m_H = S * R_H \quad \dots (14)$$

$$m_H = S / n q \quad \dots (15)$$

Where (n) is electron density and (S) is the conductivity.

Experimental part

The purified polymer were used to cast films of different thicknesses from different concentrations solution(6-10%wt/vol).The polymers were dissolved in ethylene chloride and handily shaken until a homogenous solution was obtained, after which solution was transferred to clean glass Petri dish of(7cm) in diameter placed on plate form. The dried film was then removed easily by using tweezers clamp.

The best concentration for film production for casting without bubbling and can be dismantled easily from the Petri dish was found to be 7% wt/vol.

The purified polymer, which was dissolved in the concentration stated above (7% wt/vol), was then used to prepare polymer composites in different weight ratios (5%, 9%, and13%), by mixing (0.35, 0.63.and 1.05gm) wt% of Ag with 7gm of PMMA, which is dissolved in Methylene chloride in respectively. The mixture was handily shaken until a homogenous solution was obtained, after which solution was

Evaporates, to clean glass Petri dish of (7cm) in diameter placed on plate form. The dried film was then removed easily by using tweezers clamp.

The polymer systems were evaluated spectra photometrically by using UV/160/Shimadzu spectrophotometer. Energy gap of the polymer systems (homopolymers and polymer composites) at different concentrations were plotted as a function of the weight ratio of the composites involved.

The optical constants were calculated (absorption coefficient, refractive index, extinction coefficient, and the real and imaginary parts of the dielectric constant), by using Equation (4, 7, 8, 10, and 11) for all prepared samples.

The Hall Effect was calculated concentration and motilities of the charge carriers in the polymer systems (photopolymers and polymer composites) at different concentrations using Equation (12, 14, and 15).

The prepared samples morphology was examined by using optical microscope of (Nikon-73346) with digital camera(X10).

RESULT & DISCUSSION

Ultraviolet and visible spectra for photopolymer (PMMA), and (Ag/PMMA) at different concentrations, the figure reveals a strong absorption probability below 250. For PMMA, there is sudden decrease in the absorption values shown in fig (1). For Ag/PMMA, the decrease was even slower. In the visible region (PMMA), was transparent. These results are in good agreement with Osawa, and Fukuda [16], and Aash, S.A [17].

A mixture of the preceding homopolymers was used to form the Ag/PMMA composites at different concentration.

The 13% Ag/PMMA showed the higher absorption values in comparison with other concentration, it was attributed to the increasing of localized states with increasing of silver concentration in Ag/PMMA composites [18] and [19].

The reflection spectra for photopolymer (PMMA), and (Ag/PMMA) at different concentrations, their behaviors are shown in Figure (2). It was seen that it was of the same behavior of the absorption spectra. The best reflection was for the (13% Ag/PMMA). Figure (3) shows the spectral transmittance over range of (200-400) nm for photopolymer (PMMA), and (Ag/PMMA) at different concentrations. There is sharp increasing state in (250) region in transmittance of PMMA, and for the (Ag/PMMA), the increase was lower. It is obvious that its behavior is opposite to that of the absorption and reflection spectra. The energy gap (E_g) was obtained by plotting $(\alpha hv)^{1/r}$ versus (hv) with (r) values equal to 1/2, 3/2, 2, and 3. The linear portion was best fitted with (r=1/2), which indicates a transition of direct type as in Figure (4) for photopolymer (PMMA), and (Ag/PMMA) composites at different concentrations.

The decreasing in the energy gap with increasing of (Ag) concentration in (Ag/PMMA) composites can be explained that during PMMA polymer and Ag mixing, defects formation may occur, such as voids, which give rise to desirable localized states in the band gap of the material [20-21]. The decrease in energy gap with increasing Ag concentration can be understood by considering the mobility gap variation in the doped polymer [19]. Also the decrements of (E_g) may be due to the transition between the molecular orbital, which have highest occupied molecular

orbital instead of transition between valence–conduction band gap, i.e., polymers are usually amorphous insulators so one would consider the transition between the highest occupied molecular orbital and the lowest unoccupied molecular orbital instead of a valence–conduction band gap [22].

The variation of (α) versus (λ) given in Figure (6) Shows a sharp edge for (PMMA), and (Ag/PMMA) composites at different concentrations,. For (Ag/PMMA) composites, the absorption edge shifts towards the longer wavelength side and becomes broader with Ag concentration increasing [20]. Also, it can be seen, increasing in α values in these polymer systems, is attributed to decreasing energy gap, which will be discussed. Its behavior was similar to the absorption spectra. Figure (7) shows the absorption coefficient as function of the concentration ratio, it could be seen that there was nonlinear relationship suggesting their incompatibility, which was in good agreement with Naidu, B.V. et al [20]. Figure (8) shows the variation of refractive index as a function of wavelength for the homopolymer (PMMA), and (Ag/PMMA) composites at different concentrations. It was found that the refractive index was increasing with increasing of (Ag) concentrations, that was attributed to its reflection of the highest value Figure (2) [9]. The relationship between the refractive index with concentration ratio in polymer composites. Figure (9) showed nonlinear relationship caused by its incompatibility. Figure (10) shows the variation of extinction coefficient as a function of wavelength for homopolymer (PMMA), and (Ag/PMMA) composites at different concentrations. It was seen that the extinction coefficient (k) was increasing with increasing of (Ag) concentration, so the highest extinction coefficient (k) was of (13% Ag/PMMA) and shifted towards the long wavelength. The displacement in (k) was due to the energy gap decreasing in which is the lowest (4.85 eV). Then behavior of (k) was nearly similar to corresponding absorption coefficient as shown in Figure (6).

The plots of the real part (ϵ_r) and imaginary part (ϵ_i) of homopolymer, (PMMA), and (Ag/PMMA) composites at different concentrations. The Figures (12 and 13) show that the real part behaves like the refractive index, while the imaginary part behaves like the extinction coefficient as shown in the Figures (14 and 15). The behavior of ϵ_r is similar to refractive index because the smaller value of k^2 comparison of n^2 , while ϵ_i imaginary depends on the k value, which are related to the variation of absorption coefficient. It could be concluded that 13% Ag/PMMA composites had modified the optical properties of its photopolymer. In Figure (16A) for pure PMMA, but in Figure (16 B) the continuous matrix was PMMA phase, where the Ag was dispersed phase as round particle matrix. As Ag content of composite was increased to 5%, the optical micrographs reveal the formation of an interpenetrating network or co-continuous two-phase structure Figure (16B) [18]. Figure (16C) with increase in Ag content to 9%, the compatibility of the two phases increased [23]. Figure (16D) with increase in Ag content to 13%, the more compatibility of the two phases increased.

Figure (17 and 18) show the increased concentration of carriers increased with increasing of (Ag) concentration and opposite by a decrease in mobility Hall effect of impurity scattering. Where impurity scattering dominates increasing impurity concentration and this is in line with a formula Conwell-wiskoffl [24]. Electrical resistivity versus different dopant concentrations is shown in Figure (19) the decrease

in resistivity with increase Ag concentration the rate of change mild is very due to an increase in free electron concentration as mentioned [25].

Figure (20) show the best conductivity was at 9%Ag ratio, and the lowest receptivity. The electrical conductivity increases with doping concentration.

The induced conductivity in Ag doped PMMA is shown to be dose dependent and can be attributed to the creation of induced charge carriers in the PMMA matrix. It is obvious that its behavior is opposite to that of the resistivity [26].

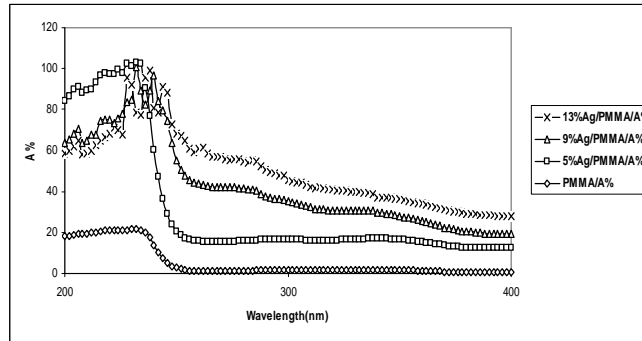


Figure (1) UV/Visible absorption spectroscopy of photopolymer, and Ag/PMMA composites at different concentration.

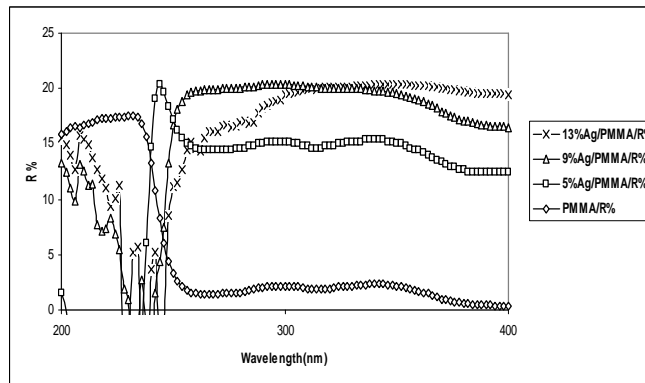


Figure (2) Optical reflection spectra of (PMMA), and (Ag/PMMA) composites at different concentration.

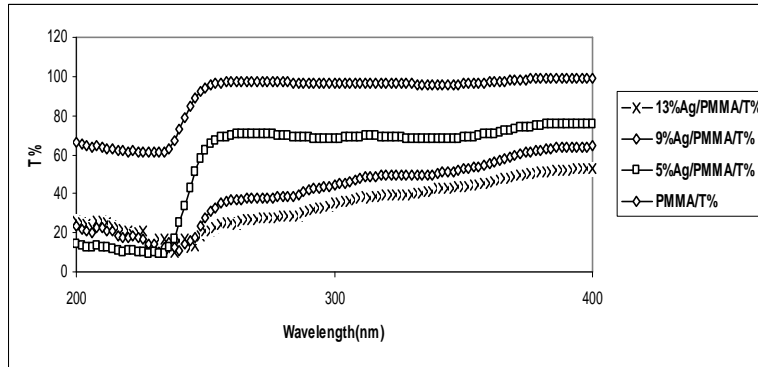


Figure (3) Optical transmittance spectra for photopolymers (PMMA), and (Ag/PMMA) composites at different concentration.

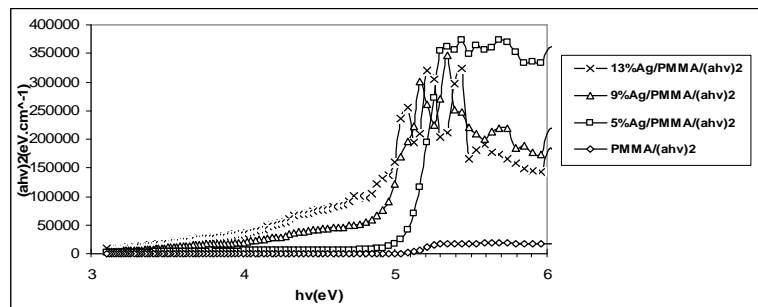


Figure (4) $(\alpha h\nu)^2$ versus $(h\nu)$ for (PMMA), and (Ag/PMMA) Composites at different concentration.

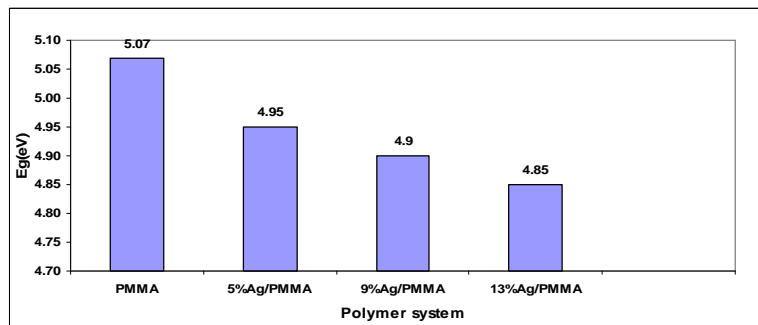


Figure (5) Energy gap values for (PMMA), and (Ag/PMMA) composites at different concentration.

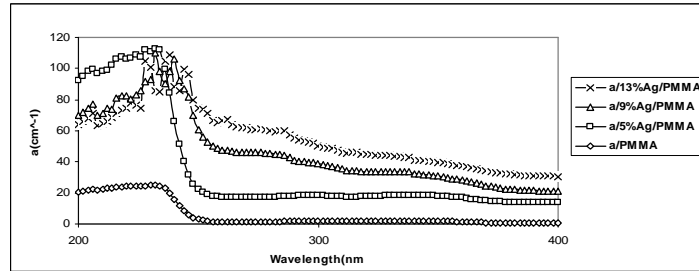


Figure (6) Absorption coefficient versus wavelength for Photopolymer (PMMA), and (Ag/PMMA) Composites at different concentrations.

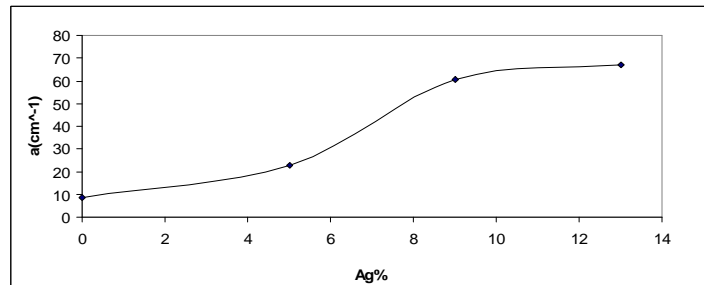


Figure (7) The absorption coefficient versus (Ag) concentration ratio.

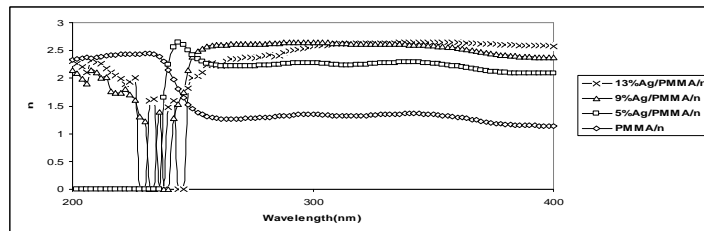


Figure (8) Variation of refractive index as a function of Wavelength for homopolymer (PMMA), and (Ag/PMMA) composites at different concentrations.

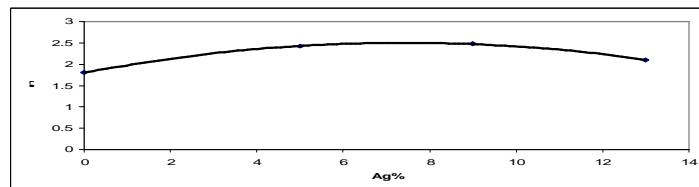


Figure (9) Variation of the refractive index versus the concentration ratio.

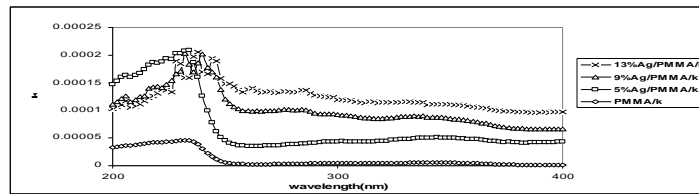


Figure (10) Variation of extinction coefficient as a function to the wavelength for PMMA, and Ag/PMMA composites at different concentration.

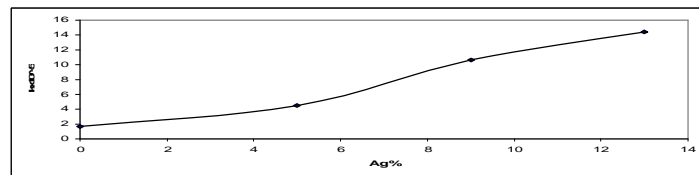


Figure (11) Variation of extinction coefficient versus to the concentration ratio.

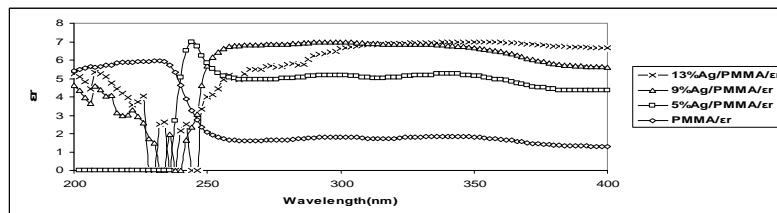


Figure (12) Variation of the real part of the dielectric Constant as a function to the wavelength for (PMMA), and (Ag/PMMA) Composites at different concentrations.

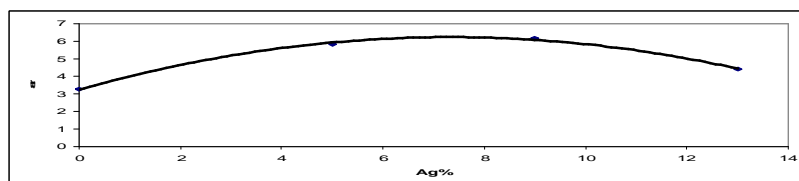


Figure (13) Variation of the real part of the dielectric Constant versus to the concentration ratio.

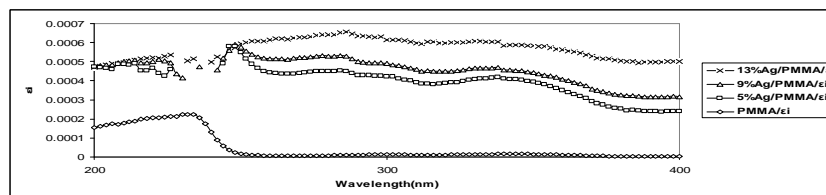


Figure (14) Variation of the imaginary part of the dielectric Constant as a function to the wavelength for (PMMA), and (Ag/PMMA) composites at different concentrations.

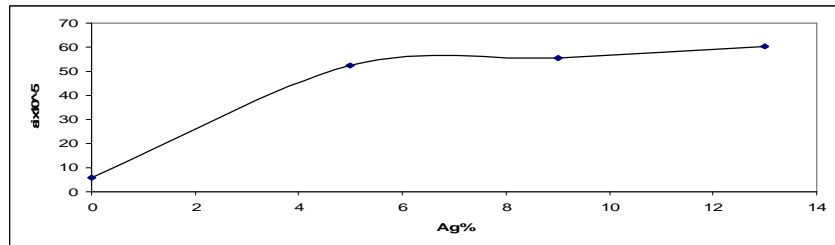


Figure (15) Variation of imaginary part versus concentration ratio.



(A) PMMA



(B) 5% Ag/PMMA



(C) 9% Ag/PMMA



(D) 13% Ag/PMMA

Figure (16) Optical micrographs of pure PMMA,
and Ag/PMMA at different concentration (X10).

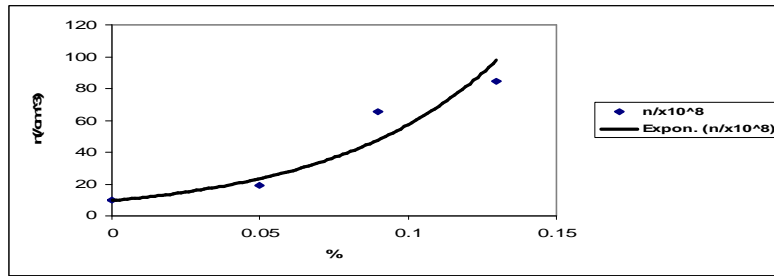


Figure (17) Variation of the concentration of carriers versus to the concentration ratio.

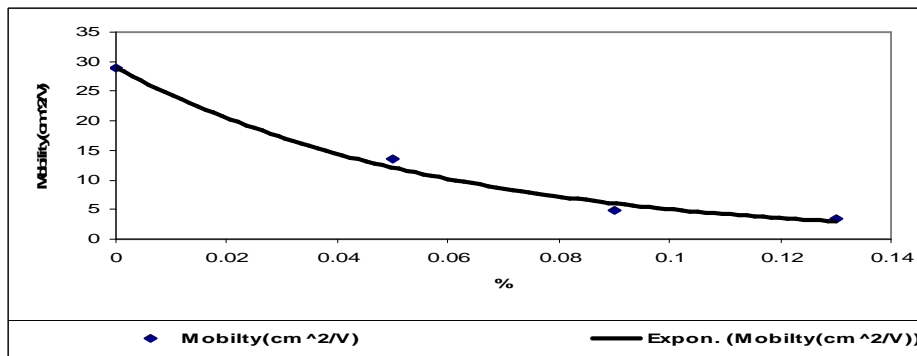


Figure (18) Variation of the mobility hall versus to the concentration ratio.

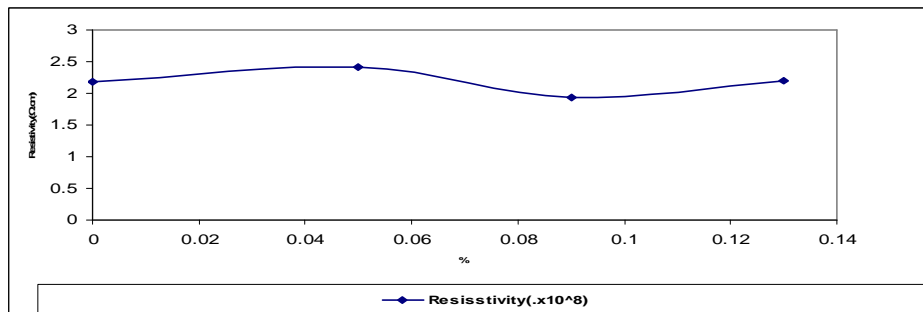


Figure (19) Variation of the resistivity versus to the concentration ratio.

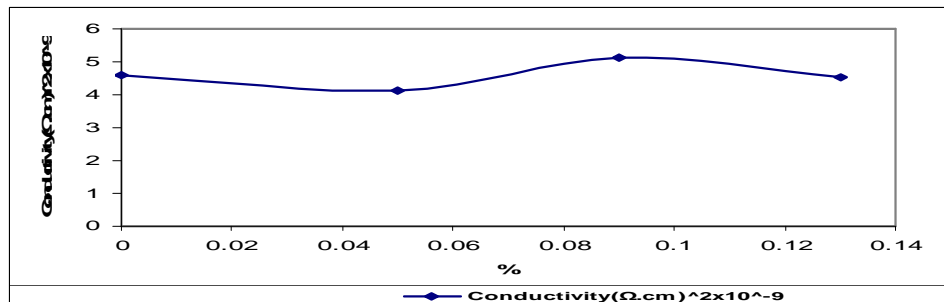


Figure (20) Variation of the conductivity versus to the concentration ratio.

Table (1) represents the parameters of optical properties of polymer system involved.

Polymer. system	E_g (ev)	λ_{cut} (nm)	n	$K \cdot 10^{-5}$	e_r	$e_i \cdot 10^{-5}$	α (cm ⁻¹)
PMMA %	5.07	244.6	1.8	1.65	3.3	5.95	8.5
5%Ag/PMMA	4.95	250.5	2.4	4.5	5.84	21.8	22.66
9%Ag/PMMA	4.9	453.1	2.8	10.64	6.2	57.5	55.8
13%Ag/PMMA	4.85	255.7	2.1	14.4	4.41	60.5	71.28

Table (2) represents the parameters of electrical properties of polymer system involved.

Polyme r. system	n/x10 ^{^8}	Mobilty(cm ^{^2} /V)	Resisstivity(.x10 ^{^8})	Conductivity(Ω.cm) ^{^2x10^{^-9}}
0	9.8	29	2.18	4.58
5%	19.2	13.5	2.42	4.14
9%	65.7	4.86	1.94	5.13
13%	84.8	3.34	2.2	4.54

دراسة تأثير تركيز الفضة على الخواص البصرية والكهربائية لمتراكب (Ag/PMMA)

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