



Fabrication of Novel (PMMA-Al₂O₃/Ag) Nanocomposites and its Structural and Optical Properties for Lightweight and Low Cost Electronics Applications



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Abstract

In this paper, preparation new type of nanocomposites may be considered as promising materials for different electronic and optical applications such as solar cells, sensors, electronics gates, transistors, lens, lasers ..etc . The nanocomposites were prepared with different concentrations of polymethylmethacrylate (PMMA), aluminum oxide (Al₂O₃) nanoparticles and silver (Ag) nanoparticles are (PMMA_{0.98-(Al₂O₃)_{0.02})_{1-x}/Ag_x where x=.0, 0.02, 0.04 and 0.06. The structural and optical properties of (PMMA-Al₂O₃-Ag) nanocomposites have been studied. The optical properties of nanocomposites were examined in wavelength range (220-820)nm. The results of optical properties for (PMMA-Al₂O₃-Ag) nanocomposites showed that the absorbance, absorption coefficient, extinction coefficient, refractive index, imaginary and real dielectric constants and optical conductivity of (PMMA-Al₂O₃) nanocomposites are increased with the increase in silver nanoparticles concentrations while the transmittance and energy band gap decrease with increase of the Ag nanoparticles concentrations. The results showed that the (PMMA-Al₂O₃-Ag) nanocomposites are promising for different optoelectronics applications.}

Keywords: Al₂O₃, optical properties, PMMA, optoelectronics, nanocomposites

In recent years, polymeric materials has gained widespread attention by the scientific and technological researchers, because of their important manufacturing applications. This materials play today a very great role in numerous fields of everyday life due to their unique advantages over conventional materials (e.g. wood, clay and metals) such lightness, resistance to corrosion, ease of processing and little cost manufacture. Also, the physical properties of polymers might be influenced by doping spending various materials as additives. Like additives are used in polymers for a variety of reasons, for example: improved processing, density control, optical effects, thermal conductivity, control of the thermal expansion, electrical properties that enable charge dissipation or electro-magnetic interference shielding, magnetic properties, flame resistance and improved mechanical properties, for instance hardness, elasticity and tear resistance[1-6]. Overall poly (methacrylates) are polymers of the esters of methacrylic acid. The most commonly used among them is poly (methyl methacrylate) PMMA. Poly

(methyl methacrylate) PMMA is one of the earliest and top known polymers, with chemical formula (C₅H₈O₂)_n[7-9]. PMMA is naturally transparent and colorless polymer with density (1.15-1.19 g/cm³), and available on the market in both pellet (granules) and sheet form under the names Plexiglas, Acrylite, Perspex, Plazcryn, Acryplast, Altuglas, Lucite etc. Polymethylmethacrylate is commonly called acrylic glass or simply acrylic[10-12]. PMMA as a polymer waveguide has attracted widely attention for use as optical constituents and in optoelectronic devices because of its extraordinary properties, such as, excellent mechanical properties where PMMA is one of the hardest thermoplastic and is also highly scratch resistant, very suitable for electrical engineering purposes and it is dielectric properties is very good, thermal capability where polymethylmethacrylate is resistance to temperature changes is very good, displays unique optical properties, simple synthesis and low cost, high transparency in the visible region, possible to use in nonlinear optics[14-18]. The expansion of new polymers, blends, composites and

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advanced materials befits requisite for alteration of mechanical, electrical, optical and thermal properties to accomplish the necessary characteristics. Composite materials because of these different properties are successfully used in nearly all areas of manufacturing and science [19-22]. One advantage of nanoparticles, as polymer additives appear to have is that compared to traditional additives, loading necessities are quite low. Microsized particles used as strengthening agents scatter light, like this reducing light transmittance and optical clarity. Effective nanoparticle dispersion combined with good polymer particle interfacial adhesion eliminates scattering and allows the exciting likelihood of developing strong yet transparent films, coatings and membranes [23]. Optical properties of polymers constitute a significant feature in study of electronic transition and the possibility of their application as optical filters, a cover in solar collection, selection surfaces and green house. The study of properties for composites or nanocomposites such as electrical, dielectric and optical properties [24-34] to use it for different application: antibacterial [35-39], pressure sensors [40-43], humidity sensors [44-48] and thermal energy storage and release [49-54]. In this paper, preparation of novel (PMMA-Al₂O₃/Ag) nanocomposites and studying their structural and optical properties for lightweight and low cost electronics applications.

1. Materials and Methods

The nanocomposites of (PMMA-Al₂O₃-Ag) are prepared by casting method by dissolving 0.98 gm of PMMA in 20 ml of chloroform then add 0.02 gm of Al₂O₃ nanoparticles. The silver nanoparticles were added to (PMMA-Al₂O₃) with different concentrations are (2, 4, 6) wt.% by using magnetic stirrer for 1 hour to obtain more homogeneous solution. The spectrophotometer's double beam (Shimadzu, UV-1800 A) was used to measure the optical properties of (PMMA-Al₂O₃-Ag) nanocomposites in wavelength 220-820 nm. The (PMMA-Al₂O₃-Ag) nanocomposites samples were examined through using the optical microscope [supplied from Olympus name (ToupView) type (Nikon-73346)] with magnification (10×). FTIR spectra were examined in wavenumber range (1000-4000) cm⁻¹ by FTIR (Bruker company, German origin, type vertex-70). The relationship between absorbed light intensity (*I*) by material and the intensity of incident light (*I*₀) is given by equation [55]

$$I = I_0 e^{-\alpha t} \dots\dots\dots (1)$$

Where (*t*) is the thickness of the matter and (α) is the absorption coefficient.

$$\alpha (\nu) = 2.303 \log \left(\frac{I_0}{I_t} \right) \dots\dots\dots (2)$$

Where the amount of $\log(I/I_0)$ symbolizes the absorbance (*A*).

The absorption coefficient (α) is defined as the capability of material to absorb light of the given wavelength can be calculated by [56]:

$$\alpha (\nu) = 2.303(A/t) \dots\dots\dots (3)$$

Where (*t*) is the thickness of the sample.

The relationship between the optical energy gap (*E_g*), absorption coefficient (α) and the photon energy (*hν*) can be written as [55,56]

$$\alpha h \nu = B (h \nu - E_g^{opt})^r \dots\dots\dots (4)$$

Where (*B*) is a constant related to the properties of the valance band and conduction band, the exponent (*r*) is an empirical index which determines the type of optical transition and can be assumed to have values of (1/2, 3/2, 2 and 3) depending on the nature of the electronic transition responsible for the absorption. *r* = 1/2 and 3/2 for direct allowed and forbidden transition respectively, *r* = 2 and 3 for indirect allowed and forbidden transition respectively [55,57].

The refractive index (*n*) of a material is the ratio of the velocity of light in vacuum to that of the specimen, and can be measured by using the following equation [1,56]:

$$R = \frac{(n - 1)^2}{(n + 1)^2} \dots\dots\dots (5)$$

$$n = \frac{(1+R)^{1/2}}{(1-R)^{1/2}} \dots\dots\dots (6)$$

The extinction coefficient (*k*) can be defined as the amount of energy losing as a result of interaction between the light and the charge of medium, and can be calculated by the following relation [58]

$$K = \alpha \lambda / 4\pi \dots\dots\dots (7)$$

Where (λ) is the wavelength. The extinction coefficient (*k*) is directly proportional to the absorption coefficient as seen from Eq.(7).

The complex dielectric constant ($\epsilon^* = \epsilon_1 + i \epsilon_2$) characterizes the optical properties of the solid material, where (ϵ_1) real part and (ϵ_2) imaginary part of the dielectric constant, and can be calculated by the following relations [58]:

$$\epsilon_1 = n^2 - k^2 \dots\dots\dots (8)$$

$$\epsilon_2 = 2 n k \dots\dots\dots (9)$$

The real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric constant are related to (*n*) and (*k*) values as seen from Eq. (8) and Eq. (9). The calculation of these two parts supply information about the loss factor.

The optical conductivity is defined using the equation [21]:

$$\sigma = \frac{\alpha n c}{4\pi} \dots\dots\dots (10)$$

2. Results and discussion

The FTIR spectroscopy was used to consider the nature the interactions between PMMA and (PMMA- Al_2O_3 -Ag)nanocomposites.

Silver nanoparticles concentrations are produced variations in spectral of (PMMA- Al_2O_3) which comprise change in the intensities and shift in some bonds. These changes credited to communications of nanoparticles with polymer. FTIR studies showing that there is no interactions between (PMMA- Al_2O_3) and Ag nanoparticles as shown in figure 1. Figure 2 shows the variation of absorbance for (PMMA- Al_2O_3 -Ag) as a function of wavelength, within the mountain range (220–820) nm for all sampling under probe. The figure demonstrations that the absorption for all samples of nanocompositerises at UV region, due to the excitement of electrons from valance band to the conduction band at these energies and the high absorbance of samples for nanocomposites at UV region credited to the energy of photon sufficient to interact with atoms. generally, It has been discovered that the absorbance reduces with increasing wavelength intended for all samples of nanocomposites. This physically means that will an incident photon has not been able in order to excite the electron and even transfer it from valance band to the conduction band because the energy of incident photon is less than the value of the energy gap value of the semiconductor. Generally typically the absorbance of all samples of nanocompositeshas reduced values in the visible and near infrared region. When the wavelength reduced, the interaction between incident photon and material will occur, and the absorbance will increase[59-62]. Also it can be observed the absorbance increases as nanoparticles percentage increases because the energy gap will decrease as samples ofnanocomposite increase.

Figure 3 shows the optical transmittance as a function of wavelength in the range (220–800) nm for pure and nanocomposites. The optical transmission values decrease along with the increases of Ag nanoparticles concentration. This kind of behavior may be as a result of the increase in free electrons with the increase in Agnanoparticles concentration[63,64].

The absorption coefficient of nanocomposites is computed by using equation (3). Figure 4 illustrations the variant of absorption coefficient for (PMMA- Al_2O_3 -Ag) nanocomposites as a function of photon energy of the incident light correspondingly. As shown in typically the figure, that absorption coefficient of most samples for (PMMA- Al_2O_3 -Ag) nanocomposites is big at high energies. This revenues that the electron transition has high probability; i.e. the energy of incident photon will be sufficient to transit typically the electron from the donor levels to the acceptor levels

which as the consequence the energy of the incident photon is larger than the energy band gap. The absorption coefficient contributions in order to know the nature involving electron transition . When the values in the absorption coefficient of material are big $\alpha > 10^4 \text{ cm}^{-1}$, the electron transmission is probable to be direct transition of electron but the electron transmission will be probable to be indirect transition if the values of the absorption coefficient of material are usually minimal $\alpha < 10^4 \text{ cm}^{-1}$. The values of absorption coefficient of (PMMA- Al_2O_3 -Ag)nanocomposites are low ($\alpha < 10^4$) cm^{-1} ; the transition of electron is indirect. The absorption coefficient of nanocomposites increases with the increasing of the concentrations of nanoparticles, this is ascribed to the increasing of number of charge carriers, hence, increase the absorbance and absorption coefficient of (PMMA- Al_2O_3 -Ag) nanocomposites. With increasing of nanoparticles concentrations, the absorption coefficient of nanocomposites increases and this is due to the increasing of number of charge carriers as shown in Figures 5 and 6, therefore, increase the absorbance, absorption and decreases the transmittance coefficient for (PMMA- Al_2O_3 -Ag) nanocomposites[65].

The energy band gap of nanocomposites is calculated by using equation(4). The energies gaps for allowed indirect transitions of (PMMA- Al_2O_3 -Ag) nanocomposites are displayed in figure 7. The energies gaps for forbidden indirect transitions of (PMMA- Al_2O_3 -Ag) nanocomposites are shown in figure 8. As is shown in the figures, the energies gaps for allowed and forbidden indirect transitions of nanocompositesare decreased with the increasing of the Ag nanoparticles concentrations, this performance is due to the making of levels in the energy gap; the transition of electron in this instance is conducted in two stages that include the transition from the valance band to the local levels in energy gap and to the conduction band as a result of increasing the Ag nanoparticles concentrations; the electronic conduction depends on nanoparticles concentrations[66].

The refractive index is calculated by using equation (6). The refractive index of (PMMA- Al_2O_3 -Ag) nanocompositesas a function of wavelength is shown in Figure 9. As shown in the figure, the refractive index of nanocomposites increases with the increasing of the Ag nanoparticles concentrations; refractive index is decreased with the increase of the wavelength. This performance ascribed to the increase of the density of nanocomposites[67]. When the incident light interrelates with a sample has high refractivity at UV region, hence, the values of refractive index will be increased. Typically the extinction coefficient can get calculated by using equation (7). Figure 10 shows the variant of (k) like a

functionality of wavelength for the (PMMA-Al₂O₃-Ag) nanocomposites, in general, it will be clear that the extinction coefficient (k) decreases along with increasing of wavelength (λ) for all samples of (PMMA-Al₂O₃-Ag) nanocomposites [68-70]. Furthermore the figure shows that will the extinction coefficient rises with increasing Ag nanoparticles concentration. This kind of behavior can be acknowledged to the increasing associated with carrier density which approves the increasing within the absorption coefficient with Ag nanoparticles concentration and that leads to raise the extinction coefficient along with Ag concentration. The extinction coefficient associated with nanocomposites has great values at UV region, this kind of behavior attributed to higher absorbance of all samples of nanocomposites. Also, extinction coefficient of nanocomposites raises with the increasing associated with the wavelength at visible and near infrared regions which ascribed to the absorption coefficient of nanocomposites is nearly constant at visible and near infrared region, hence, the extinction coefficient increases with the raising of the wavelength according to equation of extinction coefficient.

Both real (ϵ_1) and imaginary (ϵ_2) dielectric constant are measured for prepared films by using relations (8) and (9) respectively. Figure 11 shows the variation of real dielectric constant (ϵ_1) as a function of wavelength for (PMMA-Al₂O₃-Ag) nanocomposites. Figure 12 shows the influence of Ag nanoparticles concentration on the imaginary part of dielectric constant (ϵ_2) for (PMMA-Al₂O₃-Ag) nanocomposites. It is observed that their values increase with increasing of wavelength and real dielectric constant behave like refractive index we can perceive increases in the high energies near the energy gap because the effect of extinction

coefficient is very small and the imaginary part of dielectric constant (ϵ_2) depends on extinction coefficient and behave like the extinction coefficient especially in the visible and near infrared regions of wavelength where the refractive index is approximately constant while extinction coefficient increases with the increase of the wavelength [71-74].

Figure 13 shows the variation of optical conductivity with the wavelength for (PMMA-Al₂O₃-Ag) nanocomposites. The figure show that the optical conductivity of all samples of nanocomposites are decreased with the increasing of the wavelength, this compartment ascribed to the optical conductivity depends toughly on the wavelength of the radiation incident on the samples of nanocomposites; the increase of optical conductivity at low wavelength of photon is owing to high absorbance of all samples of nanocomposites in that region, therefore, increase of the charge transfer excitations. The optical conductivity spectra showed that the samples are transmittance within the visible and near infrared regions. Also, the optical conductivity of nanocomposite is augmented with the increase Ag nanoparticles concentrations, this conduct connected to the creation of localized levels in the energy gap; the increase of Ag nanoparticles concentrations increasing the density of localized stages in the band structure, therefore, increase of the absorption coefficient accordingly increasing the optical conductivity of (PMMA-Al₂O₃-Ag) nanocomposites [75-81].

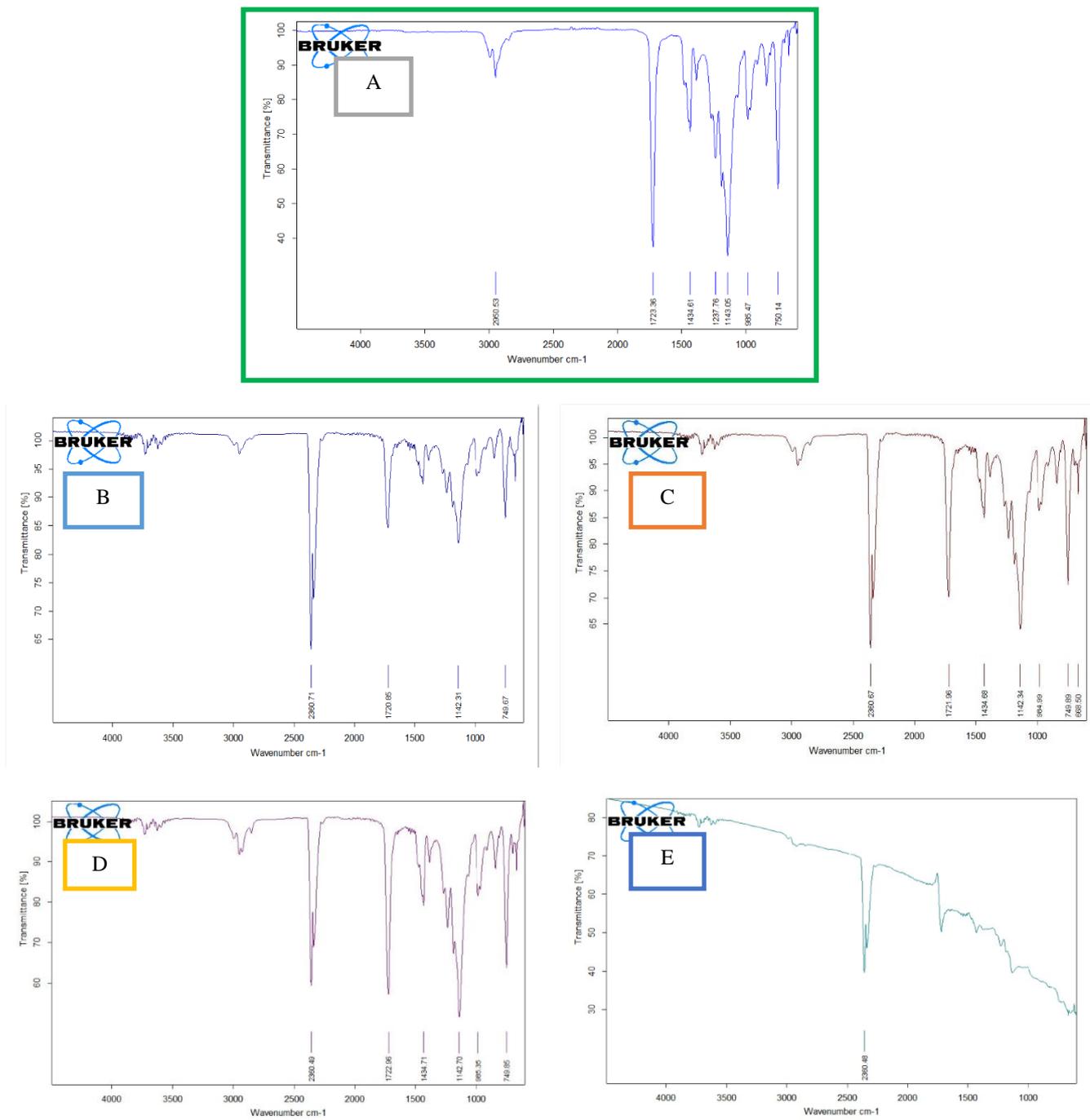


Figure 1. FTIR spectra for (PMMA-Al₂O₃-Ag) nanocomposites: A. for pure, B. for (PMMA- Al₂O₃) nanocomposites, C. for 2 wt% Ag nanoparticles, D. for 4 wt% Ag nanoparticles and E. for 6 wt% Ag nanoparticles.

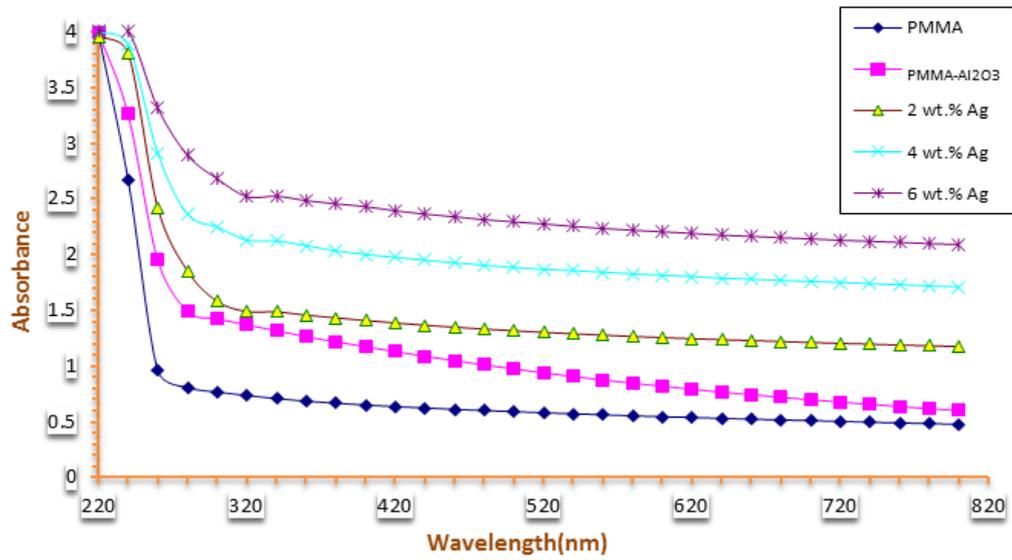


Figure 2. Absorbance as a function of wavelength for nanocomposites.

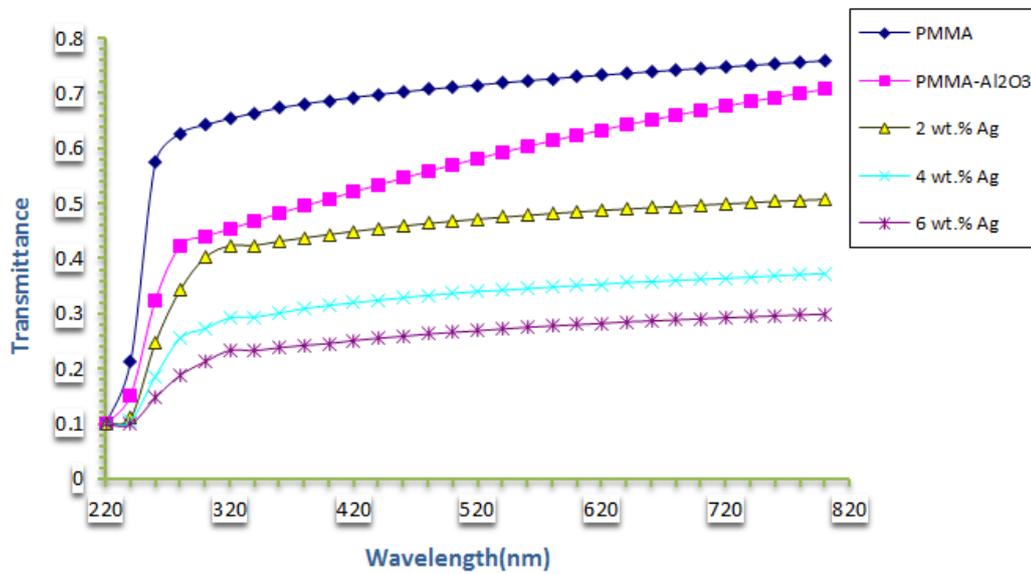


Figure 3. Transmittance as a function of wavelength for nanocomposites.

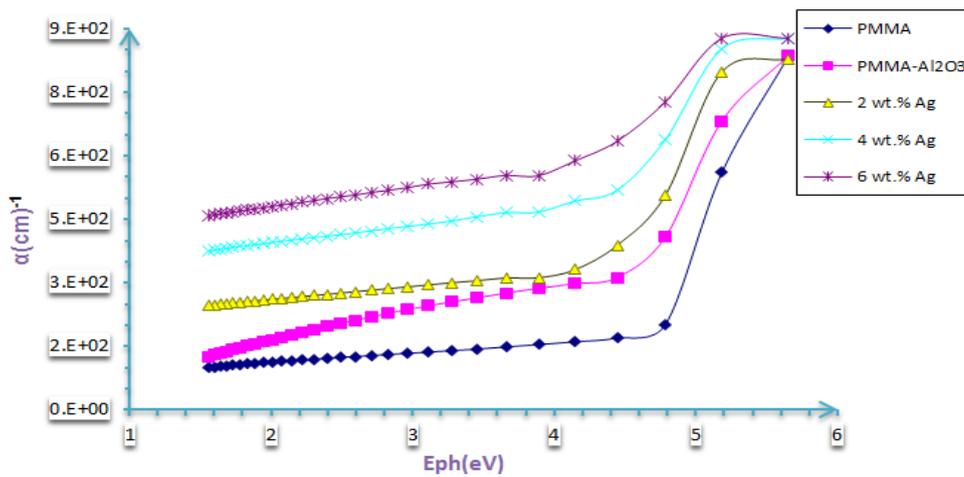


Figure 4. Variation of absorption coefficient of (PMMA- Al₂O₃-Ag) nanocomposites with photon energy.

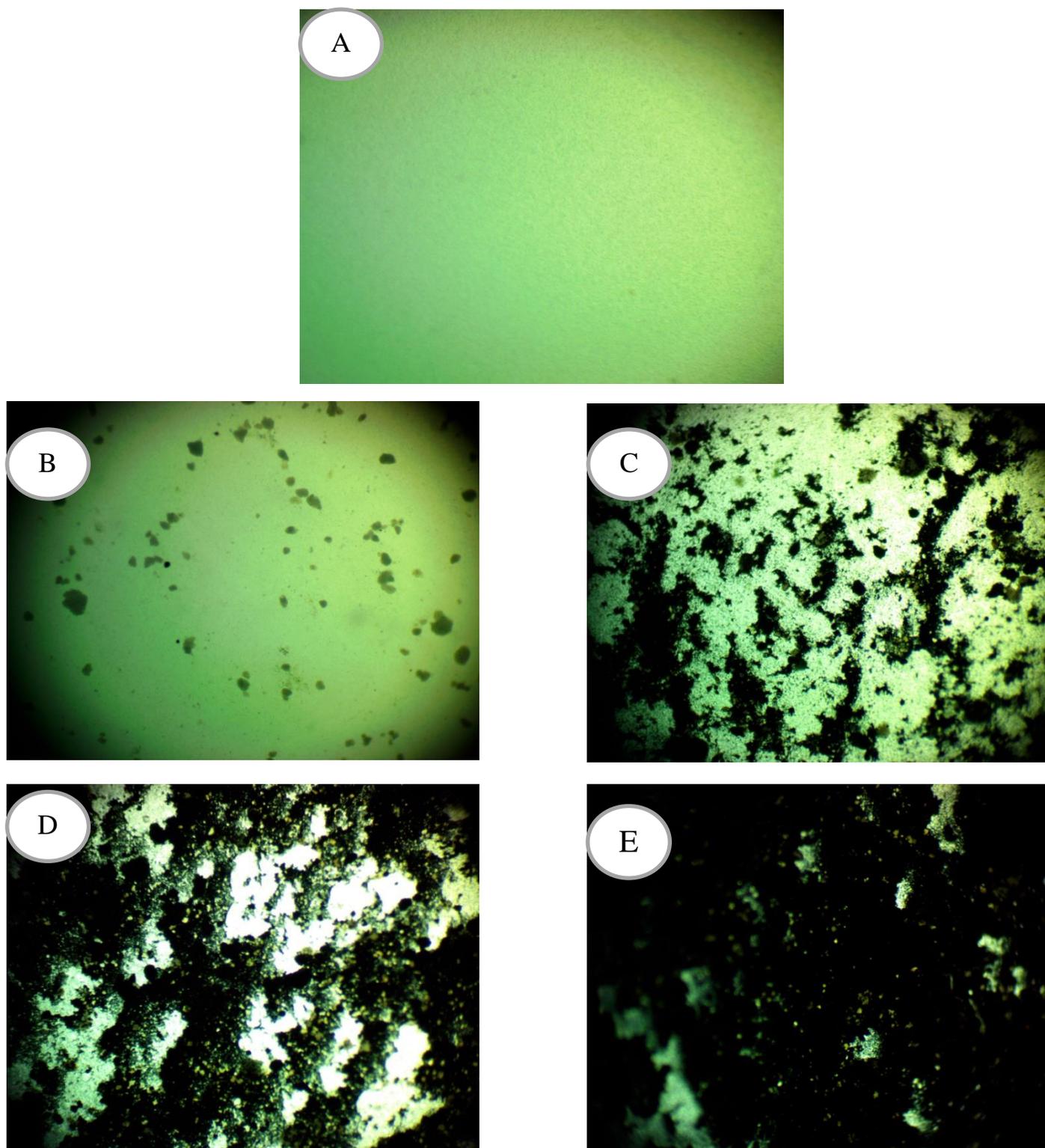


Figure 5. microscope images ($\times 10$) for (PMMA- Al_2O_3 -Ag) nanocomposites: A. for pure, B. for (PMMA- Al_2O_3) nanocomposites, C. for 2 wt% Ag nanoparticles, D. for 4 wt% Ag nanoparticles and E. for 6 wt% Ag nanoparticles.

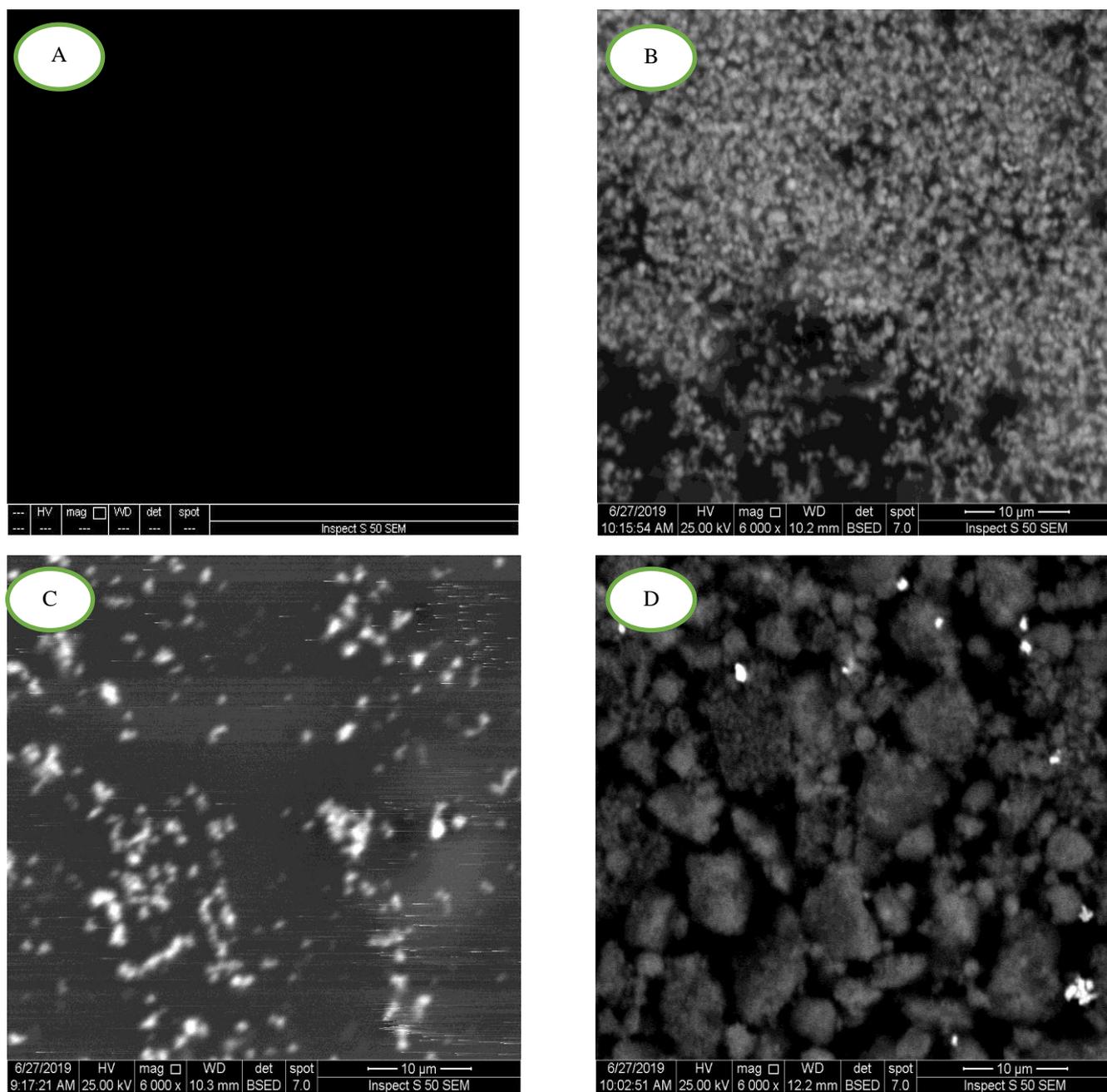


Figure 6. SEM images of (PMMA– Al₂O₃–Ag) nanocomposites: a for pure PMMA, b for (PMMA-Al₂O₃), c for 2 wt.% Ag nanoparticles and d for 6 wt.% Ag nanoparticles.

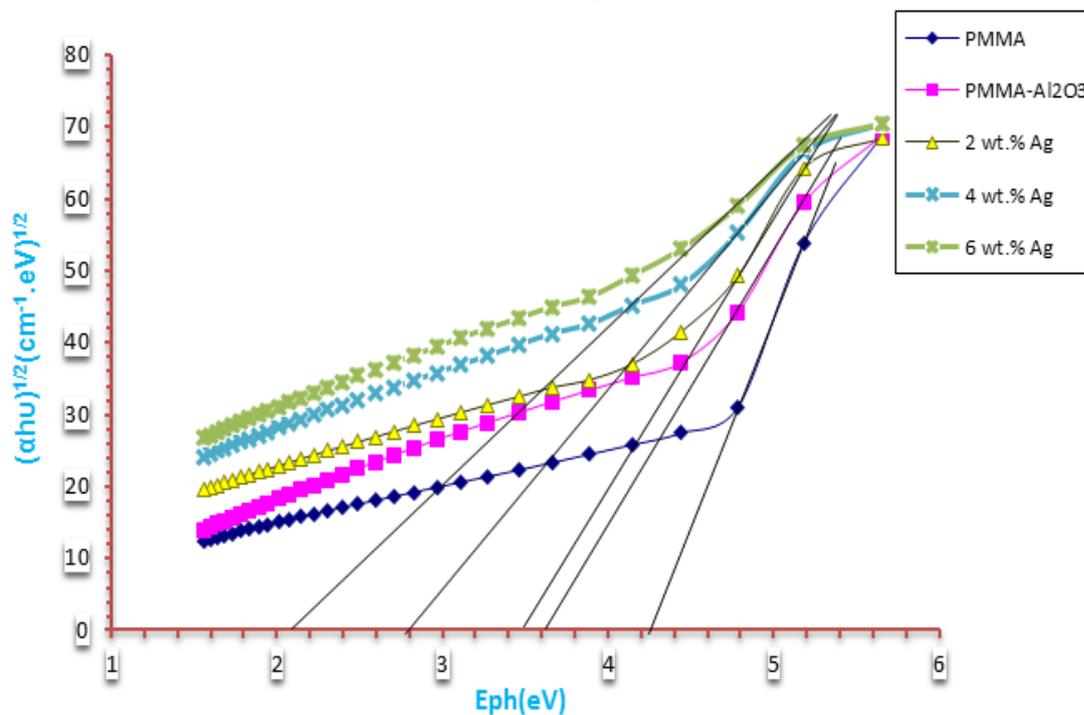


Figure 7. Variation of $(\alpha h\nu)^{1/2}$ for (PMMA- Al₂O₃ – Ag) nanocomposites with photon energy.

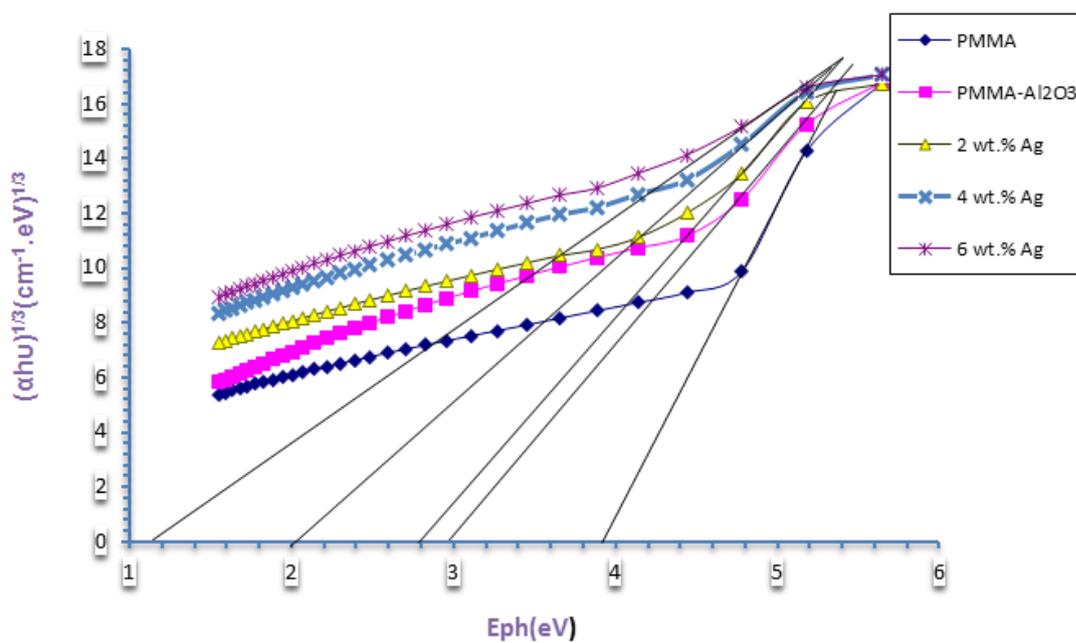


Figure 8. Variation of $(\alpha h\nu)^{1/3}$ for (PMMA-Al₂O₃-Ag) nanocomposites with photon energy.

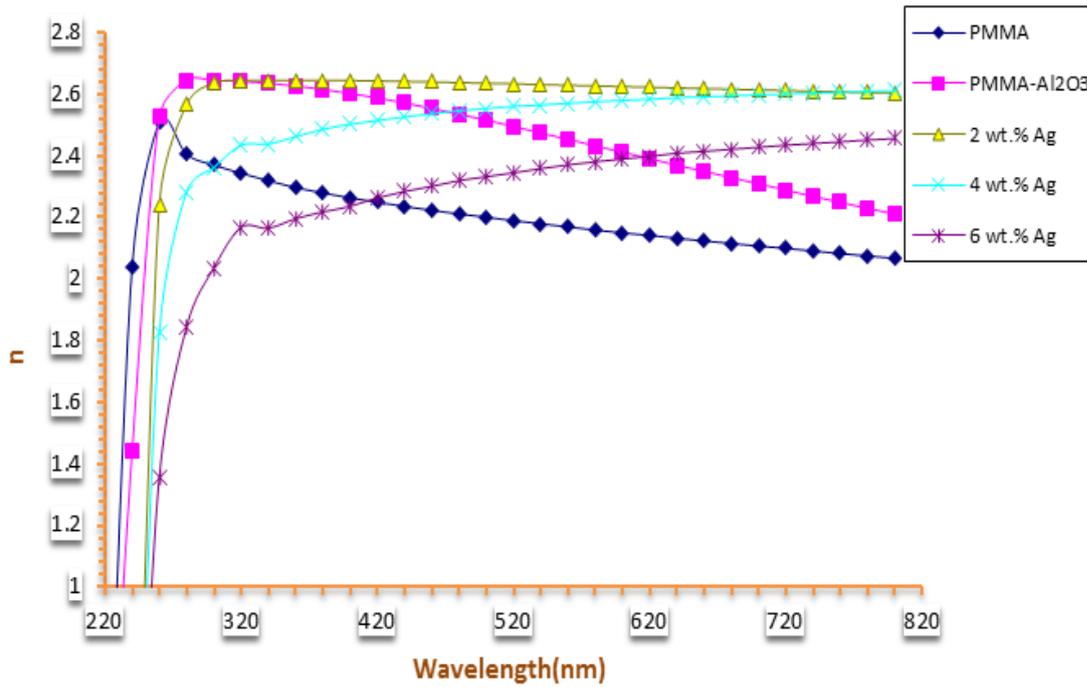


Figure 9. Variation of refractive index for (PMMA- Al₂O₃- Ag) nanocomposites with wavelength.

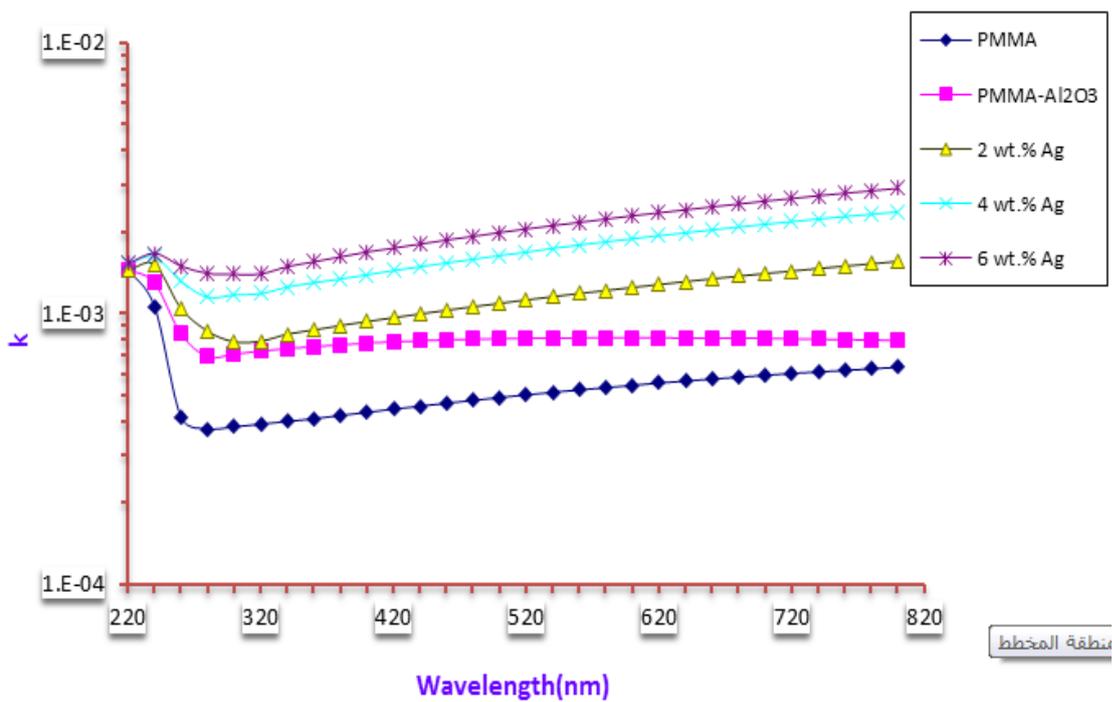


Figure 10. Variation of extinction coefficient for (PMMA-Al₂O₃-Ag) nanocomposites with wavelength.

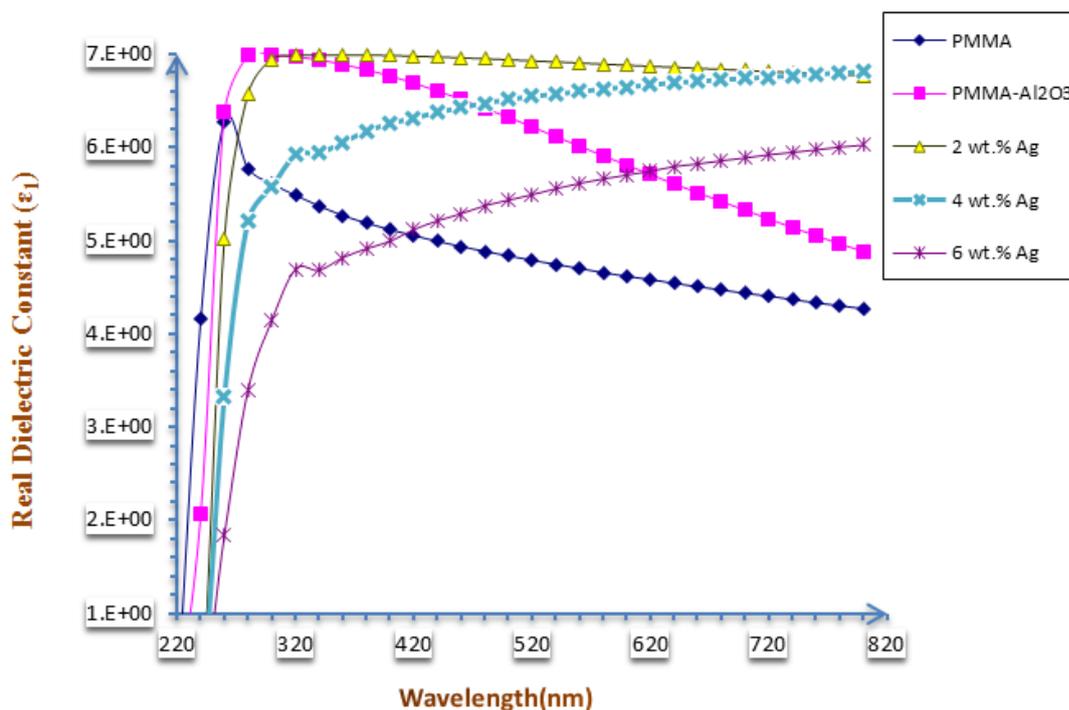


Figure 11. Real dielectric constant as a function of wavelength for nanocomposites.

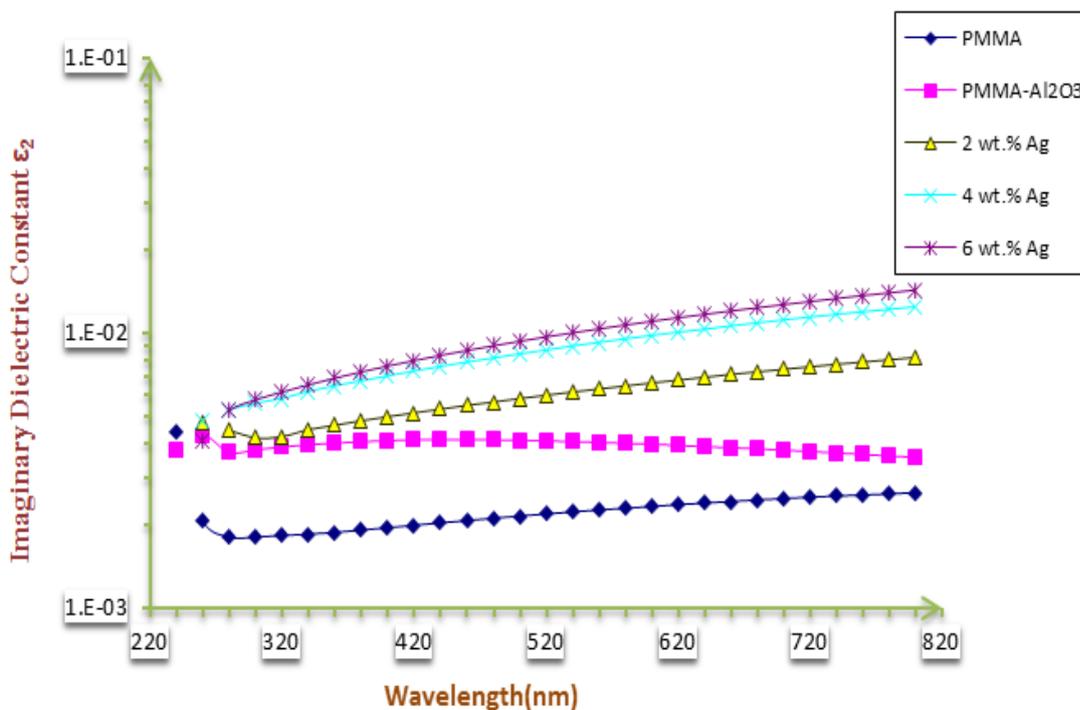


Figure 12. Imaginary dielectric constant as a function of wavelength for nanocomposites.

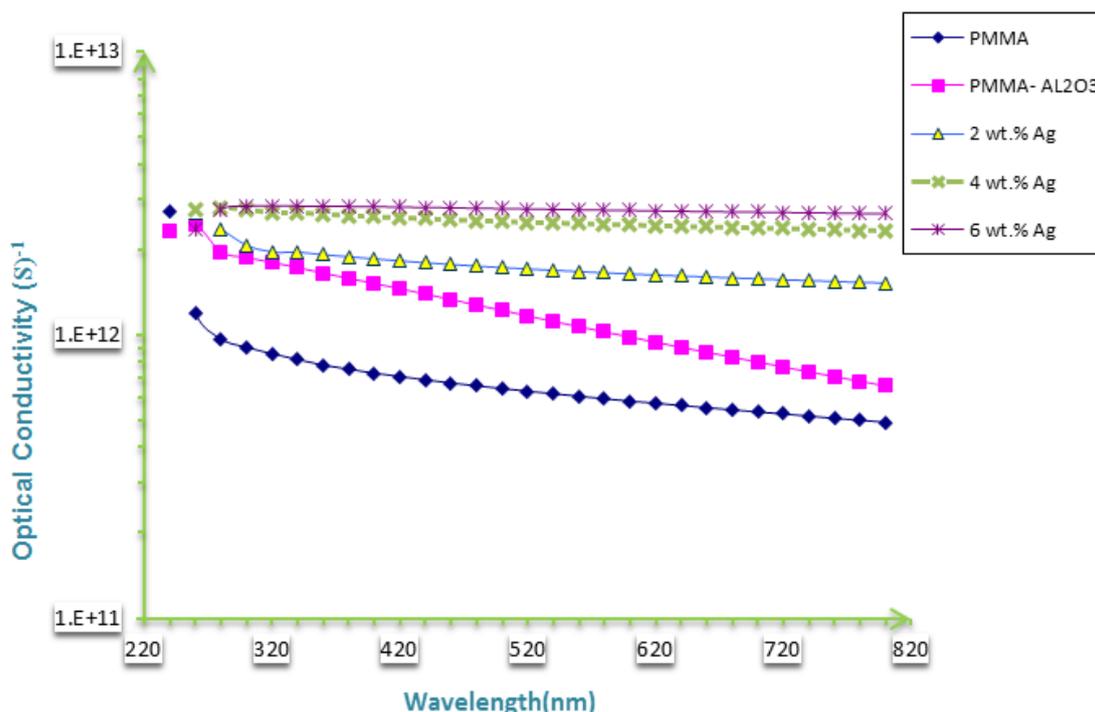


Figure13. Variation of optical conductivity for (PMMA-Al₂O₃-Ag) nanocomposite with wavelength.

3. Conclusions

The results of structural and optical properties showed that the (PMMA-Al₂O₃-Ag) nanocomposites are promising materials for different optoelectronics applications such as solar cells, sensors, electronics gates, transistors, lens, lasers ..etc . The optical absorbance of (PMMA-Al₂O₃) nanocomposites increases with the increase in Ag nanoparticles concentration. The absorption coefficient, extinction coefficient, refractive index, imaginary and real dielectric constants and optical conductivity of (PMMA-Al₂O₃) nanocomposites increase with the increase of silver nanoparticles concentrations while the transmittance and energy band gap decrease with the increase of Ag nanoparticles concentrations. FTIR studies show that there is no interactions between (PMMA-Al₂O₃) and Ag nanoparticles concentrations. Also, the (PMMA-Al₂O₃-Ag) nanocomposites have higher absorption at high energies photons and it have energy band gap 2.1 eV E_g 4.22 eV; these behaviors make it suitable for modern optoelectronics applications.

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تصنيع متراكبات نانوية مبتكرة (PMMA-Al₂O₃-Ag) وخصائصها التركيبية والبصرية للتطبيقات الالكترونية خفيفة الوزن وقليلة الكلفة

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الخلاصة

في هذا البحث تم تحضير نوع جديد من المتراكبات النانوية والتي يمكن ان تعتبر كمواد واعدة في التطبيقات البصرية والالكترونية المختلفة مثل الخلايا الشمسية، المتحسسات، البوابات الالكترونية، الترانزستورات، العدسات، الليزر، الخ.... حضرت المتراكبات النانوية بتراكيز مختلفة من بولي مثيل ميثاكريلات (PMMA) وجسيمات اوكسيد الألمنيوم النانوية (Al₂O₃) وجسيمات الفضة النانوية (Ag) هي (PMMA_{0.98}-(Al₂O₃)_{0.02})_{1-x}/Ag_x حيث x=0, 0.02, 0.04 and 0.06. درست الخصائص التركيبية والبصرية للمتراكبات (PMMA-Al₂O₃-Ag) النانوية. الخصائص البصرية للمتراكبات النانوية اختبرت في مدى الطول الموجي (220-820) نانومتر. بينت نتائج الخصائص البصرية للمتراكبات (PMMA-Al₂O₃-Ag) النانوية ان الامتصاصية، معامل الامتصاص، معامل الخمود، معامل الانكسار، ثوابت العزل الحقيقي والخيالي، والتوصيلية البصرية للمتراكبات (PMMA-Al₂O₃) النانوية تزداد مع زيادة في تراكيز جسيمات الفضة النانوية بينما النفاذية و فجوة الطاقة تقل مع زيادة في تراكيز جسيمات Ag النانوية. بينت النتائج ان للمتراكبات (PMMA-Al₂O₃-Ag) النانوية هي واعدة في التطبيقات الإلكترونية الضوئية المختلفة.