

Characterization of Silver/ Poly (Vinyl Alcohol) (Ag/PVA) Films prepared by Casting Technique

Sami S. Chiad^{*}, Saad F. Oboudi^{**}, Khalid H. Abass^{***}, Nadir F. Habubi^{*}

samichiad2003@yahoo.com, sabodi137@yahoo.com, nadirfadhil@yahoo.com

^(*) Al-Mustasiriyah University, College of Education (Ibn Hayan), Physics Department/ Baghdad/ Iraq.

^(**) Baghdad University, College of Science, Physics Department/ Baghdad/ Iraq.

^(***) Babylon University, College of Education, Physics Department.

Corresponding author's email: samichiad2003@yahoo.com, sabodi137@yahoo.com, nadirfadhil@yahoo.com

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Abstract

The optical conductivity, characteristics and optical transmittance of pure and AgNO₃-doped polyvinyl alcohol (PVA) films have been studied. The optical conductivity increased with increasing dopant concentration up to 5wt.% of the content. The increase in conductivity for dopant concentration is attributed to the formation of charge transfer complexes. Optical absorption studies in the wavelength range (300–900) nm showed peak in the wavelength region 430 nm for differently doped films, in addition to the peak for undoped PVA. The band edge values shifted to lower energies on doping up to a dopant concentration of 5wt.%.

Keywords: Optical Properties, PVA, AgNO₃-doped polyvinyl alcohol, casting technique.

INTRODUCTION

PVA is one of the earliest and best known polymers, it was seen to use in a variety of applications and is currently used extensively in semiconductor applications^[1-2]. The transmission for visible light is very high. Polymeric composites of PVA are known for their importance in technical applications^[3].

Metal/polymer composites have attracted considerable interest in recent years because of the advantageous properties of metals and polymers built into them. Studies of doping transition metal halides into PVA are important for determining and controlling the operational characteristic of the different

PVA composites^[4-6]. Since AgNO₃ is a fast conducting ion in a number of crystalline and amorphous materials, its incorporation within a polymeric system may be expected to enhance its electrical and optical performance. The incorporation of inorganic/organic material is believed to remarkably improve a wide range of properties of the polymers due to the nanosized dispersion^[7]. The addition of transition metal halides to the PVA network will cause a remarkable change in their properties^[8]. Among these properties, the enhancement of thermal property is one that has been observed in many polymer

composites ^[9]. In the study of physical properties of polymers, the optical absorption spectrum is one of the most important tools for understanding band structure, electronic properties, and optical constants of pure and doped polymers.

Many methods have been developed for the fabrication of the metal/polymer composites. However, the major disadvantages in the preparation of polymer metal composites by some methods are the poor distribution of the inorganic particle size and the poor dispersion of the inorganic particles in the polymer host and the use of toxic material for reduction of metal ^[10, 11].

The objective of this study was to synthesize and characterize the Ag/PVA composites in an aqueous solution, and to investigate the AgNO₃ dependence of some optical properties of polymer films. For this purpose the UV-Vis spectra of the composite were also studied to calculate the optical band gap energy which has been discussed in our previous paper ^[12], the Urbach parameters and some optical properties of polymer films were evaluated as a function of AgNO₃ concentration.

Experimental procedure

The PVA used as a matrix element of molecular weight 10000 g/mol. The PVA films with different amounts of silver nitrate supplied from (BDH chemicals, England) was used as a doping agent with a concentration of 3wt.% and 5wt.%, these materials were prepared by solution casting method.

A known quantity of PVA powder were added to redistilled water and ethanol and kept it for 24 hours to swell the granules with stirring the solution at 40 °C for

complete dissolution. Silver nitrate were dissolved in redistilled water and added to the polymeric solution with continuous stirring. Then the solution was poured on to a clean glass plate dishes and dried for 24 at 40°C. The thicknesses of the film were in the range of $20 \pm 0.05 \mu\text{m}$. The optical studies were carried out using double beam spectrophotometer (Shimadzu UV- probe Japan) in the wavelength range (300-900) nm.

Results and discussions

The transmittance and reflectance of pure and doped PVA polymer films recorded in the applied wavelength range are shown in Figures (1) and (2). It is clear from these figures that transmittance spectra for all films increased with increasing wavelength, while reflectance decreased. Increasing AgNO₃ content of the films decreases transmittance and increases reflectance for a lower wavelength range. This means that there is some absorption in that wavelength range. For each composition, typical spectral behavior of transmittance and reflectance are given for pure and doped PVA films.

The absorption peak maxima of the UV-Visible spectra of PVA doped with AgNO₃ were found to be red shifted as the weight concentration of AgNO₃ increases. While, the doped films with AgNO₃ solution has maximum absorption peak at 430 nm. The pure PVA show no bands in the range of measurement.

The reflectance band at 430 nm is attributed to the free electrons in the conduction bands of Ag particles. This result is in complete agreement for that Ag nanoparticles prepared by chemical reaction ^[13].

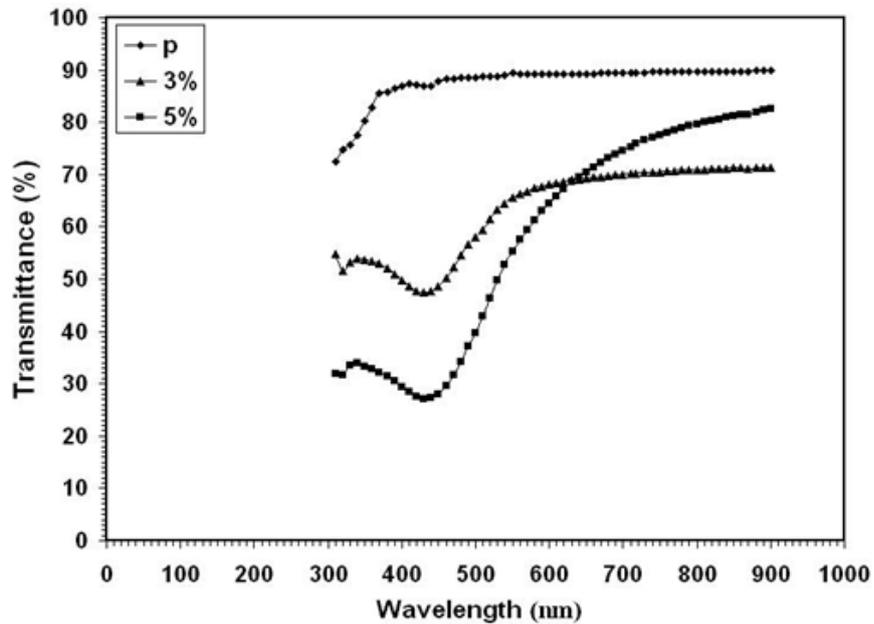


Fig. (1) Transmittance versus wavelength for the PVA and PVA:Ag films.

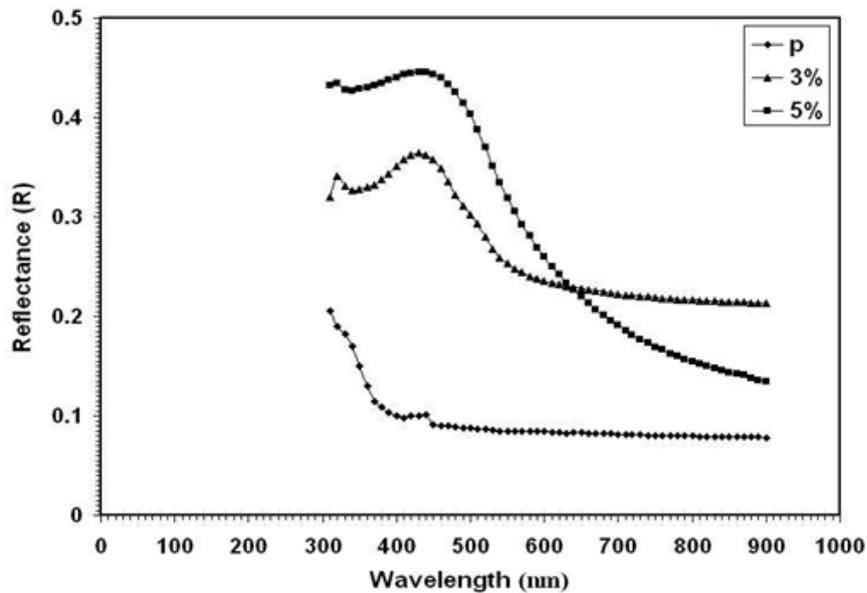


Fig. (2) Reflectance versus wavelength for the PVA and PVA:Ag films.

The absorption coefficient can be represented by the Tauc model ^[14]: $(\alpha h\nu) = B (h\nu - E_g)^f \dots \dots \dots (1)$

Where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the optical energy gap, B a constant known as the disorder parameter which is nearly independent of the photon energy and r is the parameter measuring type of transition and it suggest values of (1/2, 2, 3/2 and 3) for allowed direct, allowed indirect and forbidden direct and indirect transitions respectively, so in order to get the property of the band, we need to test the above transition where could be found that $r = 3$ fitted with our results, which has been published in our previous research^[12]. As the

doped films show a red shift behavior, it can be concluded that the presence of dopant and its interaction results in the creation of new molecular dipoles, which could be results of point defects created within the band gap. Fig. (3) Shows that the absorption coefficient was also increased as the doping concentration of $AgNO_3$ increased to 5wt.% showing a broad peak appeared at 430 nm. According to the literature, this band could be attributed to chelate formation of Ag^+ coordinated with the hydroxyl group of PVA^[15], or to silver particle formation^[16].

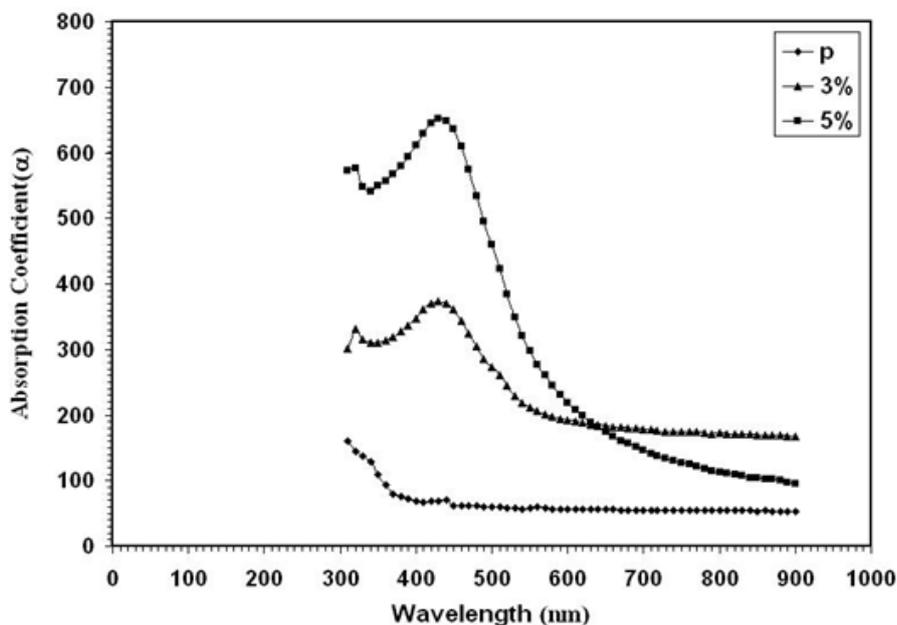


Fig. (3) Absorption Coefficient versus wavelength for the PVA and PVA:Ag films.

The width of the localized states available in the optical bandgap of the

prepared films affects the optical band gap structure and optical transitions

and it is called as Urbach tail, which is related directly to a similar exponential tail for the density of states of either one of the two band edges^[17]. The Urbach tail of the films can be determined by the following relation^[18]:

$$A = \alpha_0 \exp (E/E_U) \dots \dots \dots (2)$$

Where E is the photon energy, α_0 is constant and E_U is the Urbach energy which refers to the width of the exponential absorption edge. Fig. (4) Show the variation of $\ln \alpha$ versus photon energy for the films. This behavior corresponds primarily to optical transitions between occupied states in the valence band tail to unoccupied states at the conduction band edge. The E_U value was calculated from the slope of Fig. 4 using relationship:

$$E_U = [d (\ln \alpha) / d (h\nu)]^{-1} \dots \dots \dots (3)$$

E_U values are given in Table (1). Urbach energy values of the films increases with increasing AgNO_3 content. The E_U values change inversely with optical band gaps of the films. The decrease in E_g is attributed to the increase of disorder of the material occurred by doping. This increase leads to a redistribution of states, from band to tail, thus allows for a greater number of possible bands to tail and tail to tail transitions^[19]. As a result, both a decrease in the optical gap and a broadening of the Urbach tail occurred. It is clear that AgNO_3 dopant increases the width of the tail of localized states and decreases the energy gap of PVA films.

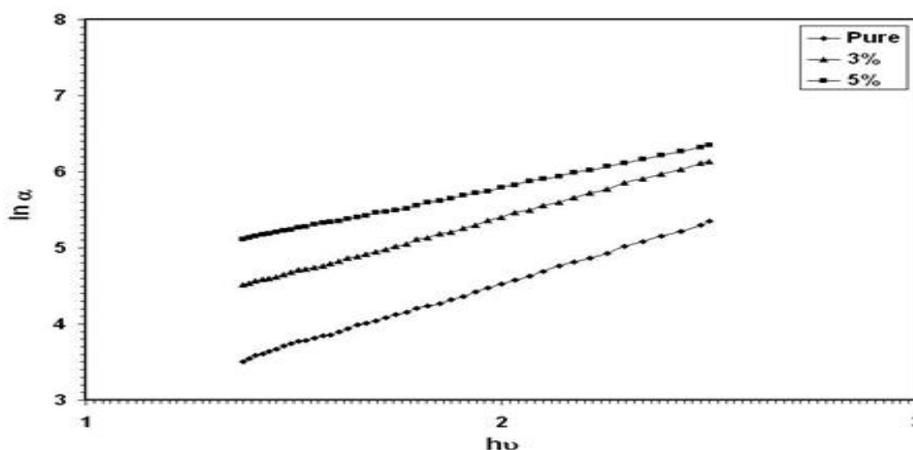


Fig. (4) $\ln \alpha$ versus photon energy for the PVA and PVA:Ag films.

Table (1) Urbach energy

Sample	Urbach energy
0 wt.% AgNO ₃ (Pure)	625 meV
3 wt.% AgNO ₃	714 meV
5 wt.% AgNO ₃	910 meV

The real (ϵ_1 and imaginary ϵ_2 parts of the dielectric constant were obtained using the formula as:

$$\epsilon_1 = n^2 - k^2 \dots\dots\dots(4)$$

$$\epsilon_2 = 2nk \dots\dots\dots(5)$$

The variation in the real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric

constant for different AgNO₃ contents are shown in Figures (5) and (6). The values of the real part are higher than those of the imaginary part. The values of real and imaginary parts of the dielectric constant at 430 nm for 0%, 3% and 5% AgNO₃ content were 4.09, 16.61 and 26.02, and 0.002, 0.012 and 0.026, respectively.

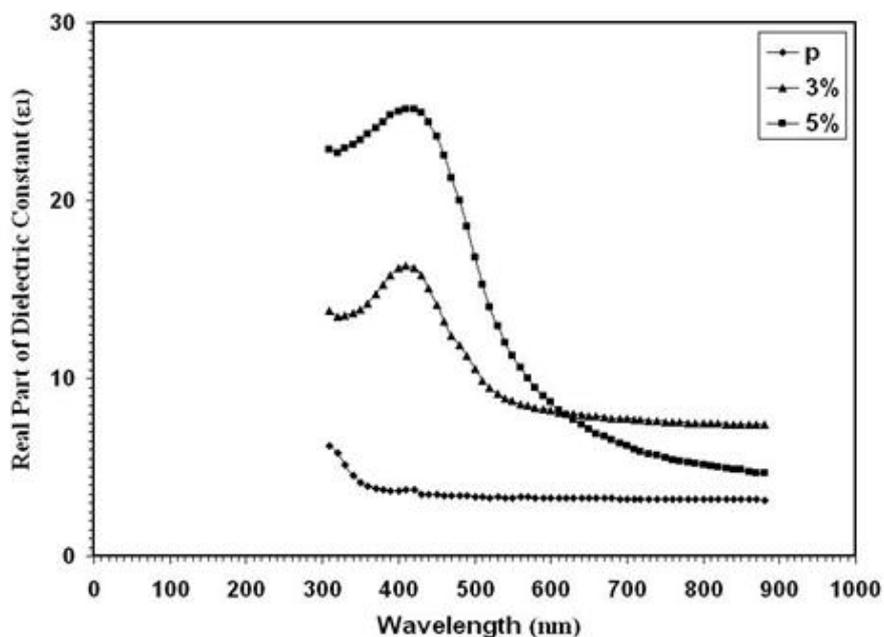


Fig. (5) The spectra of real (a) part of the dielectric constant of films

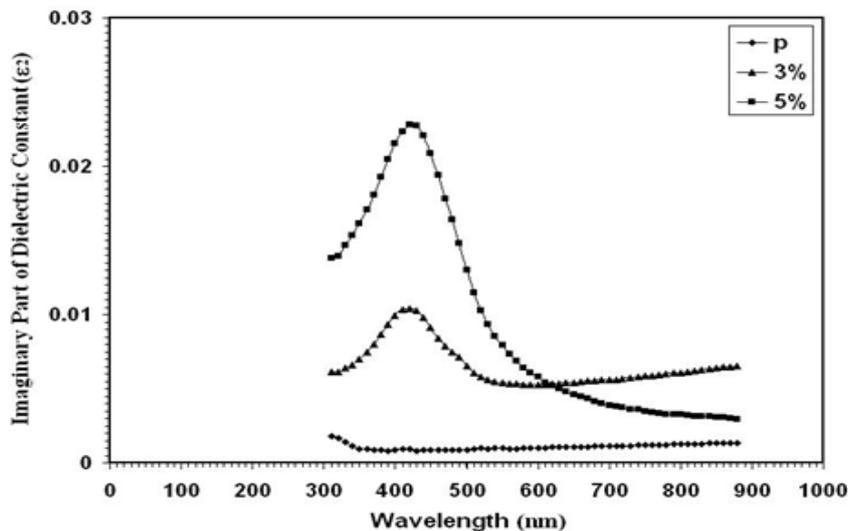


Fig. (6) The spectra of imaginary part of the dielectric constant of films

The optical conductivity was calculated using the relation ^[20]:

$$\sigma = \frac{\alpha n c}{4 \pi} \dots\dots\dots (6)$$

Where (c) is the velocity of light.

Figure (7) shows the variation of optical conductivity with the wavelength, the conductivity values of the PVA and PVA:

AgNO₃ films at room temperature. It was observed that the optical conductivity increases as the percentage of AgNO₃ in the PVA increase to 5%. The increased optical conductivity at high photon energies is due to the high absorbance of the PVA and PVA: AgNO₃ films in that region.

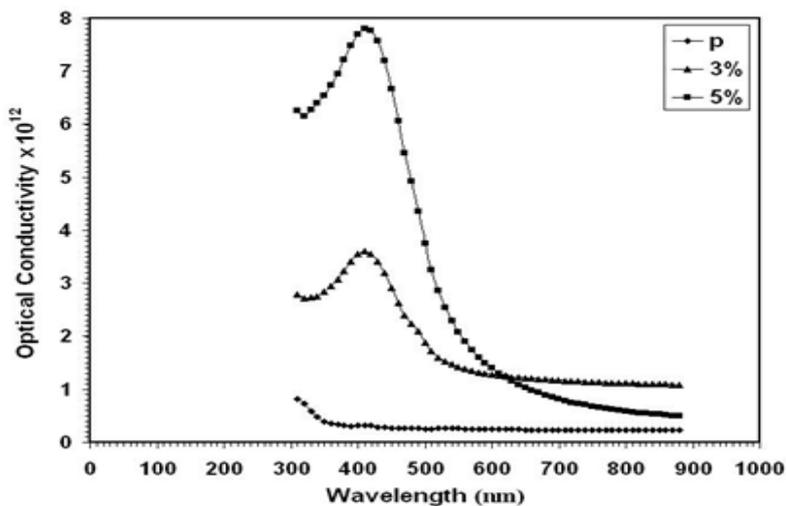


Fig. (7) Optical conductivity versus wavelength for the PVA and PVA:Ag films.

Conclusion

This result indicates that AgNO₃ can effectively dope PVA and enhance the optical properties. The improvement in the optical properties may be attributed to the doping with AgNO₃ that leads to the formation of π -electron clouds, with the polarization aligned in the direction of the molecular chains. The UV-Visible spectra of pure and doped PVA shows a peak maxima were found to be red shifted as the amount of AgNO₃ increase. The real and imaginary parts of dielectric constants and the optical conductivity of PVA were found to be increased due to AgNO₃ doping.

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