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Optical Characterization of Silver Doped Poly (Vinyl Alcohol) Films

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Abstract

Silver-doped PVA films were prepared by casting method in order to study the effect of silver on the optical properties of poly(vinyl alcohol) using UV/VIS spectroscopy. It was found that these thin films have an indirect optical band gap (2.4-1.3) eV as the doping percentage increase. Extinction coefficient and refractive index increase as the doping percentage increase, while in general the optical dispersion parameters show an opposite behavior with doping.

Introduction

Polymeric materials are of interest in scientific and technological research (Mule et al. 2004, Liu et al. 2005, Chen et al 2006) because they can be tailored to meet specific requirement for a variety of applications, this is mainly due to lightweight, good mechanical strength, optical properties (Bhajantri et al. 2006, Bulinski et al 2004).

Poly(vinyl alcohol) (PVA) is one of most important polymeric materials, because it has many applications in industry and is of relatively low cost in manufacture (El-Sherbiny et al. 2001). For instance, it can be used as a solid polymer electrolyte when doped with phosphoric acid in solid state electrochromic display (ECD), solid state photocells (Somani et al. 2000, Somani and Radhakrishnan 2001), or as a steric stabilizer for producing conducting polymer dispersion (Somani 2002).

In recent years, doped polymers have been a subject of considerable interest because their physical and chemical properties make them useful for specific applications.

In this manuscript, we examine combining the features of organic materials with those of inorganic materials, such as poly (vinyl alcohol) – silver composites, in order to study the effect of silver on some optical characteristics of the above composites.

Materials and Methods

PVA with molecular weight of 10000 g/mol (BDH chemicals England) was used as the basic polymeric

materials in this work. The PVA solution films with different amounts of AgNO₃ dopant were prepared by solution casting method. 1 g of PVA powder was added to doubly distilled water and allowed to swell for 24 h at room temperature. Silver nitrate was dissolved in redistilled water and added to the polymeric solution with continuous stirring. Then the solution was poured into flat glass plate dishes. Homogenous films were obtained after drying in an air oven for 24 h at 40 °C. The thickness of the films were in the range of 20 ± 0.05 μm.

The optical studies were carried out using double beam spectrometer (Shimadzu UV probe Japan) in the wavelength range (300-900) nm and infrared spectra were recorded using Shimadzu FTIR-8700 spectrometer in the wavelength range (400-4000) cm⁻¹ with a resolution of 4 cm⁻¹.

Results and Discussion

The Fourier Transform Infrared spectroscopy (FTIR) spectra of pure and silver nitrate doped PVA films were obtained and the results are shown in Figures 1-3. The spectra show a strong broad absorbance at 3343 cm⁻¹ for pure PVA and 3354 for 3 % and 5 % silver nitrate doped PVA. This band could be assigned to O-H stretching vibration of hydroxyl group of PVA, the band corresponding to C-H asymmetric stretching vibration occurs at 2911 cm⁻¹ and 2948 cm⁻¹ for the doped PVA. The band at 1712 cm⁻¹ corresponds to C=C stretching vibration and remains the same for 3 % dopant and shifted toward 1714 cm⁻¹ for 5 % dopant. Absorbance at 1661 cm⁻¹ corresponds to an acetyl C=O group, which could be explained on the basis of intra/inter molecular hydrogen bonding with the adjacent OH group. The sharp band 1094 cm⁻¹ corresponds to C-O stretching of acetyl groups present on the PVA backbone that remains the same for all the doped and undoped samples.

The corresponding bending, wagging of CH₂ vibrations are at 1435 and 1331 cm⁻¹ respectively (Selim et al. 2005, Shin et al. 2004, Dai et al. 2002). The shift in the corresponding bands with doping

indicates that there is an interaction between PVA and silver nitrate.

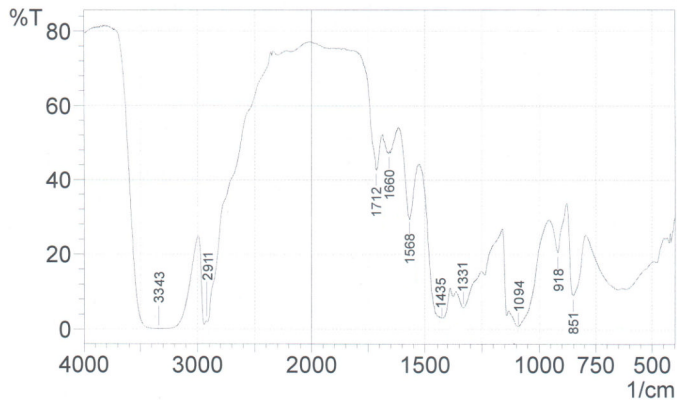


Fig. 1: FTIR spectra of pure PVA thin films.

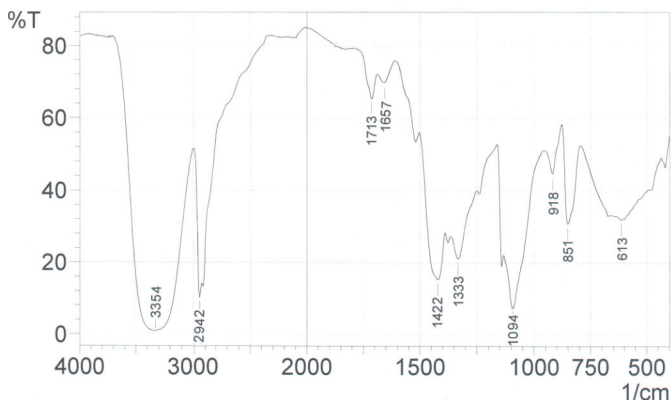


Fig. 2: FTIR spectra of 3% silver nitrate doped PVA thin film.

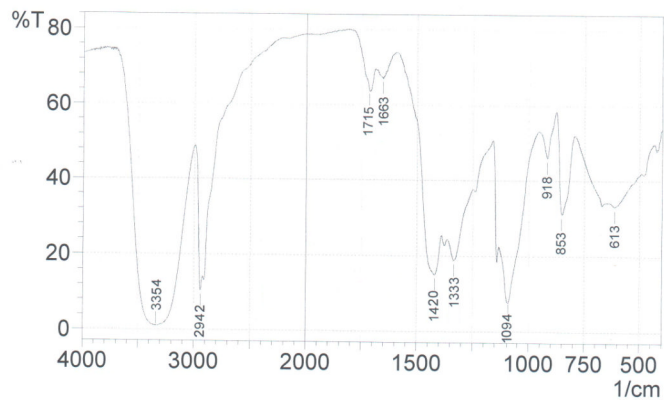


Fig. 3: FTIR spectra of 5% silver nitrate doped PVA thin film.

The UV visible spectra of the films are presented in Fig. 4.

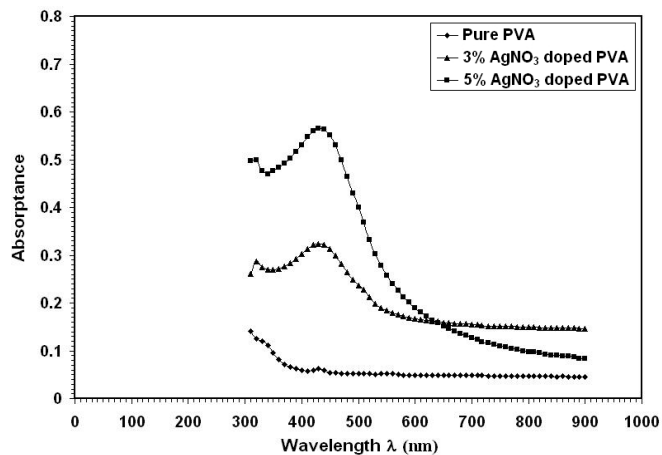


Fig. 4: Absorbance versus wavelength for pure, 3% and 5% AgNO₃ doped PVA samples

No absorption in the range 350-600 nm was observed for the undoped PVA films but as the doping percentage increase, the absorbance was also increased 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 (Zidan 1999) or to silver particle formation (Porel et al. 2005). The absorption coefficient can be represented by the Tauc model as (Zong et al. 2006):

$$(\alpha h\nu) = B (h\nu - E_g)^r \dots\dots\dots (1)$$

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.

If $r = 2$ or 3 the transition is indirect allowed and forbidden, 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. Fig. 5 shows the absorption coefficient $(\alpha h\nu)^{1/3}$ plots of PVA and AgNO₃ doped PVA films as a function of the photon energy ($h\nu$). The optical band gap is determined through extrapolating the linear portion to $\alpha h\nu = 0$. As can be seen from Fig. 5, a good linear relation is fitted with equation (1) between (2.4-1.3eV).

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.

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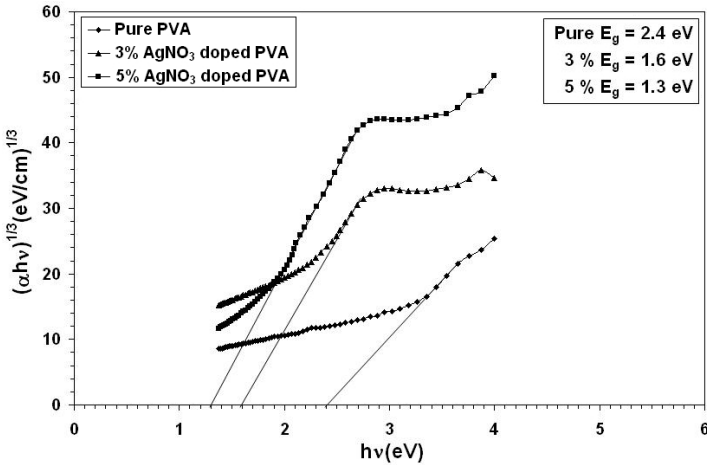


Fig. 5: $(\alpha hv)^{1/3}$ versus photon energy for pure, 3% and 5% $AgNO_3$ doped PVA samples.

The calculated value of α was used to estimate the values of the extinction coefficient (k) using the following relation (Sharma 2006):

$$k = \frac{\alpha \lambda}{4 \pi} \dots\dots (2)$$

where (α) is the absorption coefficient and (λ) is the incident wavelength.

Fig. 6 shows the dependence of k on wavelength for all the investigated films. It can be clearly seen that the extinction coefficient increase as the doping percentage increased. The same behavior was observed with refractive index (Fig. 7), which could be determined from the following relation (Abu- Sehly and Soltan 2002):

$$n = \left(\frac{1+R}{1-R} \right) \pm \left[\left(\frac{1+R}{1-R} \right)^2 - (1+k^2) \right]^{1/2} \dots\dots (3)$$

where R is the reflectance.

Wemple and Didomenico (Wemple and M. Didomenico 1971, Didomenico and Wemple 1969) used a single oscillator dispersion of the frequency dependent dielectric constant to define dispersion energy parameters E_d and E_o . This method describes the dielectric response for transitions below the optical gap, the single oscillator model below absorption edge is defined as (Wemple and Didomenico 1971):

$$n^2 - 1 = \frac{E_o E_d}{E_o^2 - E^2} \dots\dots (4)$$

where E_o is the single oscillator energy and E_d is the dispersion energy which measures the average strength of inter band optical transition. The oscillator energy is an average of optical band gap $E_o \approx 2E_g$.

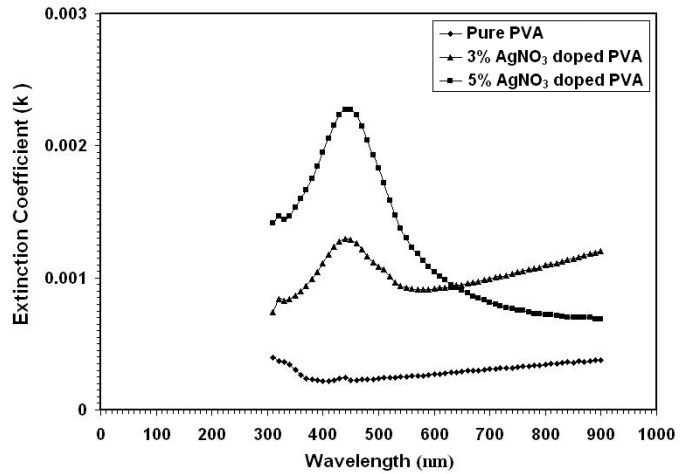


Fig. 6: Extinction coefficient versus wavelength for for pure, 3% and 5% $AgNO_3$ doped PVA films.

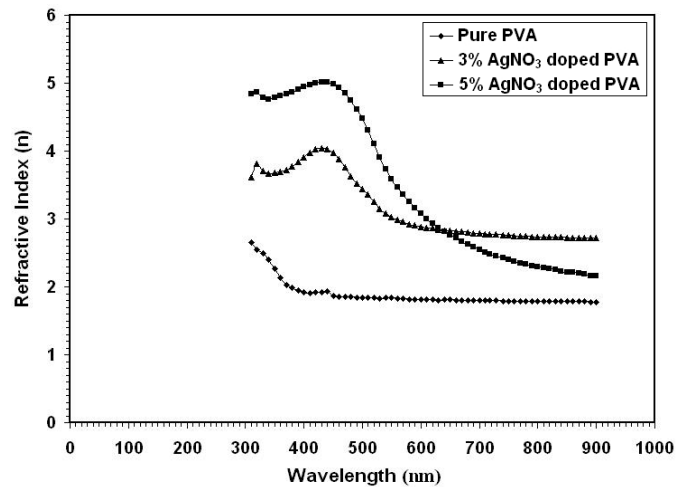


Fig. 7: Refractive index versus wavelength for pure, 3% and 5% $AgNO_3$ doped PVA samples.

Experimental verification of eq. (4) can be obtained by plotting $(n^2-1)^{-1}$ vs. $(hv)^2$ as shown in Fig 8, E_o and E_d values were determined from the slope $(E_o E_d)^{-1}$ and intercept (E_o/E_d) .

The long wavelength limit of refractive index n_∞ can be determined using the expression (Raj et al. 2008):

$$n_\infty = \sqrt{1 + \frac{E_d}{E_o}} \dots\dots (5)$$

The values obtained for the static dielectric constant $\epsilon_{\infty} = n_{\infty}^2$ are listed in Table 1.

It can be seen that all parameters affected by doping and that the value of the optical gap which determined by this model were in good agreement with the values obtained by the Tauc model.

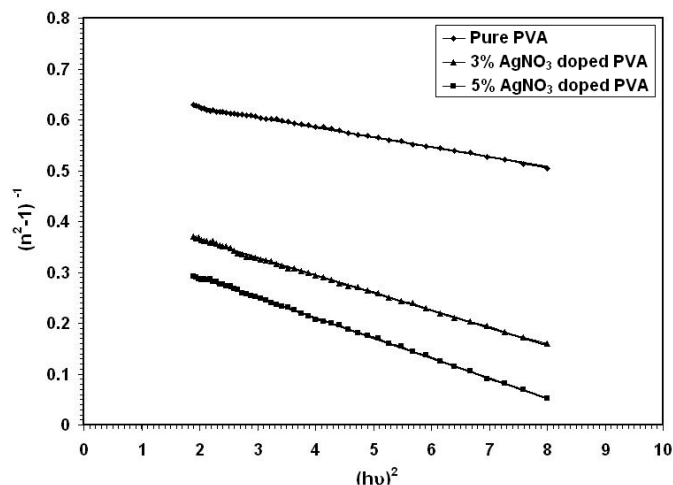


Fig. 8. $(n^2 - 1)^{-1}$ as a function of $(h\nu)^2$ for pure, 3% and 5% AgNO_3 doped PVA samples.

Table 1: The optical parameters of AgNO_3 doped PVA.

Sample	E_d (eV)	E_o (meV)	E_g (eV)	n_{∞}	ϵ_{∞}
Pure PVA	8.700	5.84	2.92	1.58	2.50
3 % AgNO_3 doped PVA	8.162	3.55	1.78	1.80	3.24
5 % AgNO_3 doped PVA	8.400	2.99	1.5	1.95	3.80

Conclusions

- 1- FTIR measurements reveal that AgNO_3 interacts with the PVA polymer, as can be seen from the shift of corresponding bands.
- 2- The AgNO_3 dopant affects the optical energy gap by reducing its value to 1.3 eV for the 5 % doping.
- 3 A single oscillator model indicates that the static refractive index increased as the dopant percentage increase and the values of E_d and E_o were determined.

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