## INTERNATIONAL JOURNAL OF RESEARCH IN PHARMACY AND CHEMISTRY

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Research Article

# OPTICAL STUDY ON NISO₄ DOPED PVA

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#### ABSTRACT

The effect of NiSO<sub>4</sub> dopant on the optical properties of poly (vinyl alcohol) has been studied. Pure and NiSO<sub>4</sub> doped PVA films were prepared using casting method. Transmission and absorption spectra have been recorded .Transmittance spectra of the films indicated that the films have high transparency. Optical absorption measurements were carried out for the samples at room temperature in the wavelength range from (200-700) nm in order to calculate the band tail width, band gap energies and the refractive indices. It was found that doping has affected all these parameters.

Keywords: PVA; optical properties; energy gap; doping.

#### INTRODUCTION

Recently, studies on optical and electrical properties of polymer films have increased enormously for their extensive applications in optical and electronic devices<sup>1</sup>. The synthesizing of these materials can be customized to have exceptional optical and electrical properties. Poly(vinyl alcohol) (PVA) is one of the most important polymeric materials as it has many applications in industry and is of relatively low cost<sup>2</sup>. PVA is a potential material having a very high dielectric strength, good charge storage capacity and dopant-dependent electrical and optical properties. Vargas et al. studied the electrical conductivity of the PVA blend with inorganic acids and water<sup>3,4</sup>. It is reported that the water content in the PVA based electrolyte enhanced the conductivity while preserving the dimensional stability of the electrolyte<sup>5</sup>. Literature studies reveal that the ammonium salts are excellent proton donors to the polymer matrix and ammonium salts doped with PVA are rare. In the present work, the effect of NiSO<sub>4</sub> on the optical properties of the PVA films was studied via determining the absorption coefficient and refractive index (n).

#### MATERIALS AND METHODS

In this work, PVA were used as basic polymeric material.Pure and NiSO<sub>4</sub> doped PVA samples were prepared at room temperature using casting method. The aqueous solution of this polymer was prepared by dissolving PVA in distilled water and heated gently in water bath to prevent thermal decomposition of polymer and thoroughly stirred for about one hour at room temperature until PVA was completely soluble.

Different concentration of NiSO<sub>4</sub> i.e. (0.1, 0.3, 0.5, 0.7, 1%) were dissolved in distilled water and added to the polymer solution, heated for a while until completely dissolved. The solution poured on to a glass plate and left to dry for 24 hr to remove any residual solvent. The thickness of the produced films were measured by using indicating micrometer and ranged (0.13 - 0.41) µm.

The optical absorbance (A) of the samples were measured as function of wavelength ( $\lambda$ ) in the wavelength range from (200-700) nm by using computerized Shimadzu UV-VIS 160 spectrophotometer full scale absorbance up to (2.5).

#### **RESULTS AND DISCUSSION**

The study of the optical absorption spectra is one of the most productive methods in developing and understanding the structure and energy gap of amorphous nonmetallic materials. Figure 1 presents the absorption spectrum of pure and NiSO<sub>4</sub> doped PVA.Itis obvious that the absorption increases as the doping percentage of NiSO<sub>4</sub> increases. The absorption coefficient ( $\alpha$ ) has been calculated for all samples from the following relation:

$$\alpha = 2.303 \text{ A/d}$$
 (1)

Where (A) is the absorption and (d) is the film thickness.

Figure 2 shows the absorption coefficient of pure and doped PVA. The width of the localized states available in the optical band gap affects the optical band gap structure and optical transitions and is called Urbach tail, which could be determined by the following relation<sup>6</sup>:

$$\alpha = \alpha_{o} \exp(E/Eu) \qquad \dots (2)$$

Where E is the photon energy,  $(\alpha_o)$  is a constant and Eu is the Urbach energy which refers to the width of the exponential absorption edge. The values of Eu were calculated as the reciprocal gradient of the linear portion of the plot.

Figure 3 and 4shows the variation of In $\alpha$  versus photo energy for undoped and doped PVA films with different thickness, the value of Eu were calculated from the slope and the obtained value are listed in Table 1,which indicates that Urbach energy values decrease with the increasing doping ratio. This variation leads to a redistribution of states from band to tail, thus allows for a greater number of possible band to tail and tail transitions<sup>7</sup>.

The optical energy band gap is determined by translating the spectra into Tauc's plots<sup>8</sup>. To translate the absorption spectrum in to Tauc's plot, we use the frequency dependent absorption coefficient given by Mott and Devis<sup>9</sup>:

$$\alpha E = B(E - Eg)r \qquad (3)$$

where B is a constant and the exponent (r) is an empirical index, which is equal to 2, 3, 1/2, and 3/2, depending on the nature of electronic transition responsible for the absorption . The plot of the product of absorption coefficient and photon energy  $(\alpha hu)^2$  versus the photon energy hu at room temperature shows a linear behavior, which can be considered as an evidence for direct transition<sup>8</sup>. Extrapolation of the linear portion of this curve to a point  $(\alpha hu)^2 = 0$ gives the optical energy band gap Eg for the PVA films with different doping concentration. Figures 5 and 6 show the band gap for the PVA films with  $NiSO_4$  concentration (pure) and (0.7) respectively. Here, the transition between the valence and conduction bands is assumed to be direct transition. The figure shows that the band gap increases with the increase of the doping concentration.

The calculated values of energy gap are listed in Table 1 as in above for different concentrations of (PVA) blend. It can be noticed that by increasing the concentration of (NiSO<sub>4</sub>) in the blend, the values of Eg increased but dropped to their minimum value at the (0.7) of (NiSO<sub>4</sub>) concentration. While the values of Urbach energy Eu decreased by increasing (NiSO<sub>4</sub>) in the blend. This behavior can be attributed to the effect of internal potential fluctuation associated with the structural disorder <sup>9</sup>.

The refractive index is a suitable state parameter directly correlated to the material density. Figure 7 shows the variation of the refractive index of PVA and PVA+ NiSO<sub>4</sub> samples. It is clear from this figure that the refractive index influenced by the doping concentration of Ni-SO<sub>4</sub>. The refractive indices of these samples decrease with the increase of the NiSO<sub>4</sub> concentration which is a result of decreasing the number of atomic refractions due to the increase of the linear polarizability. This result is in agreement with Lorentz formula<sup>11</sup>, as in equation (6)

$$[n^2 - 1] / [n^2 + 2] = (4/3) \pi N \alpha_P$$
 (6)

Where n, N, and  $\alpha_P$  are refractive index, the number density of molecules, and linear polarizability, respectively. In addition, the decrease in the values of the refractive index for different concentration of (NiSO<sub>4</sub>) could be attributed to localized density increased arising from photo induced cross linking<sup>10</sup>. The refractive index (n) can be determined from the reflectance (R) using the relation<sup>11</sup>:

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - K^2}$$
(7)

### CONCLUSION

The calculated values of the optical parameters illustrated that there was a reduction in Eg value of the films by increasing the concentration of NiSO<sub>4</sub> to (0.7) in the blend.Also, the refractive index values have been calculated from a combination of reflectance and absorbance measurements at normal incidence for all films which illustrated that there was a decrease of this values by increasing the concentration of NiSO<sub>4</sub> to (0.7) in the blend. In conclusion, from all the previous results, it could be concluded that (0.7) of  $NiSO_4$  in PVA blend has modified the optical properties of its homopolymers. This may suggest that they could be good matrices for the dyes used in fluorescent solar collectors.

#### ACKNOWLEGMENT

This work has been supported by the Department of Chemistry, College of Science, Al-Nahrain University and the College of Engineering and Computing, Al-Ghurair University, Dubai, UAE.



Fig. 1: The absorption spectrum of pure and doped PVA



Fig. 2: The absorption coefficient of pure and doped PVA



Fig. 3: Lna VsE(eV) for pure PVA



Fig. 4: Lnα VsE(eV) for PVA doped 0.7%NisO<sub>4</sub>







Fig. 6: The energy gap for PVA doped 0.7%NisO<sub>4</sub>



Fig. 7: The refractive index Vs concentrations

Т	able 1	: Th	e calc	ulated	values	of
er	nergy	gap	Eg, Uı	bach e	energy	Eu
			_	_		

NiSO₄ %	Eg	Eu	n		
0	5.71	0.427	1.51		
0.1	5.90	0.228	1.5		
0.3	5.92	0.197	1.49		
0.5	5.85	0.149	1.48		
0.7	5.20	0.073	1.47		
1	6.02	0.063	1.51		

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