

## Effect of NaI doping on some physical characteristic of (PVA)<sub>0.9</sub>-(KHSO<sub>4</sub>)<sub>0.1</sub> composite films

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### Abstract

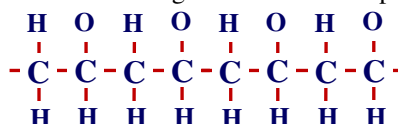
Electrolyte composite films of Polyvinyl alcohol (PVA)<sub>0.9</sub> filled with potassium hydrogen sulfate (KHSO<sub>4</sub>)<sub>0.1</sub> with different concentration of sodium iodide (NaI) were prepared using solution caste technique. The absorption spectral analysis data were carried for the samples to determine the influence of NaI contents, the obtained data showed that the direct allowed optical energy gap of the films decreases from **6.316 eV** to **4.964 eV** with increasing NaI contents up to **20%** weight. Furthermore, in order to understand the behavior of electrical conduction in these composite, the alternating electrical conductivity and dielectric permittivity have been investigated for different concentration of NaI at temperature range (**300 – 350**)K over the frequency ranging from **10KHz** to **1MHz**. The electrical conductivity of the composite increased with increasing temperature and it obeys power law  $A\omega^s$  in which s is in the range of **0.3 < s < 0.7**.

**Keywords:** Electrolyte composite, Optical constants, Dielectric constant, Energy gap, Electrical conductivity.

### 1. Introduction:

Studies on electrical and optical properties of polymer electrolyte have aroused blooming attraction due to their widely applications in electronic devices and optical devices like solar cells, fuel cells, solid state batteries, [1] and also exhibits promising medical technological applications [2].

The high dielectric strength (good insulating material), good charge storage capacity as well as the low electrical conductivity and high flexibility make the Poly-vinyl alcohol (PVA) as an exceptional polymer for microelectronic industry [3]. PVA has a carbon chain backbone with hydroxyl groups attached to methane carbon; see Fig. (1). These OH groups can be a source of hydrogen bonding, assist the formation of polymer electrolytes and plays an important role in determining the chemical and physical properties of PVA [4].



Fig(1): The structure of polyvinyl alcohol.

Electrical conduction in polymers has been extensively studied in recent years to understand the nature of charge transport in these materials. Various conduction mechanisms such as Schottky effect, the Pool-frenkel effect, space charge limited conduction and hopping conduction have been suggested for the charge transport [5]. In general, the conduction depends on the thermally generated carriers and also on the addition of suitable additives [1,6]. Inorganic additives such as transition metal salts have a considerable effect on the optical and electrical properties of PVA polymer [3,4], especially using sodium metal ion as fillers attribute to its availability in abundance of a cheaper coast than the other alkali metals like Lithium. Furthermore, softness of the material makes it easier to achieve a good contact with other component as in a battery [7]. Many researchers were studied [1,8,9] the optical band gap and tail of localized state which are the fundamental parameters of an optical material which are closely related to the electronic properties of the material.

The present work was devoted to investigate the effect of KHSO<sub>4</sub>, and NaI on some characteristics of polyvinyl alcohol (PVA) films, including the optical band gape energy, and dialectical properties.

### 2. Optical Energy Gap:

The valuable information such as the electronic band structure and the optical energy band gap can be obtained from the absorption coefficient. The absorption coefficient  $\alpha(\nu)$  can be estimated from the optical absorption spectrum owing to the following equation [10].

$$\alpha(\nu) = 2.303 \frac{A}{d} \quad (1)$$

where  $\nu$  is the frequency, and absorbance  $A$  is defined by  $\log(I_0/I)$  of the film thickness  $d$  in cm, where  $I_0$  and  $I$

are the intensities of the incident and transmitted beams respectively. When the photon energy  $h\nu > E_{opt}$  (the optical energy band gap), the present optical data have been analyzed at the near edge optical absorption according to the relationship [8,11]:

$$\alpha(\nu) = \frac{\beta(h\nu - E_{opt})^r}{h\nu} \quad (2)$$

here  $\alpha$  is the absorption coefficient,  $h$  is Planck's constant, the value of  $\beta$  is given by

$$\beta = \frac{4\pi\sigma_0}{nc\Delta E} \quad (3)$$

where  $\sigma_0$  is the extrapolated  $dc$  conductivity,  $\Delta E$  is energy gap tail (or energy which is interpreted as the width of the tail of localized states in the forbidden band gap),  $n$  is the refractive index. The value of  $r$  determines the type of electronic transition causing the optical absorption as follows [12]:

$$r = \begin{cases} r = \frac{1}{2} & \text{(direct allowed transition)} \\ r = \frac{3}{2} & \text{(direct forbidden transition)} \\ r = 2 & \text{(indirect allowed transition)} \\ r = 3 & \text{(indirect forbidden transition)} \end{cases}$$

The optical energy band gap  $E_{opt}$  estimated from the plotting of  $(\alpha h\nu)^{1/r}$  versus  $h\nu$ . On the other hand, if the photons of energy  $h\nu < E_{opt}$ , the absorption of photons is related to the presence of localized tail states in the forbidden gap.

### 3. Electrical Measurements:

The dielectric constant  $\epsilon'$ , and dielectric loss factor  $\epsilon''$  of sample were calculated using the following relations[13]:

$$\epsilon' = \frac{C_s d}{\epsilon_0 S} \quad (4)$$

$$\epsilon'' = \frac{\sigma_{ac}}{\epsilon_0 \omega} \quad (5)$$

here  $C_s$  is a capacitance, which were measured using the LCR meter.  $S$  is the effective cross-sectional area of the sample,  $\epsilon_0$  is permittivity of free space ( $8.85 \times 10^{-12}$  F/m),  $\sigma_{ac}$  is the  $ac$  conductivity of the sample that arises from the motion of charge carriers through the polymer, and  $\omega$  is the angular frequency. The measured conductance  $G_s$  was used to calculate  $\sigma_{ac}$  using the following expression [3,14]:

$$\sigma_{ac} = \frac{d G_s}{S} \quad (6)$$

In general the complex impedance  $\sigma^*$  was written as  $\sigma^* = \sigma'(\omega) + i\sigma''(\omega)$  where  $\sigma'$  and  $\sigma''$  are the real and imaginary parts of the conductance. The real part of conductivity  $\sigma'$  has been often analyzed separated in two different components [15,16]:

$$\sigma' = \sigma_{dc} + \sigma_{ac} \quad (7)$$

where  $\sigma_{dc}$  is the  $dc$  conductivity, which is frequency independent conductivity [17], while the  $ac$  conductivity  $\sigma_{ac}$  is frequency dependent and follows a universal power law in the form of [3,8]:

$$\sigma_{ac}(\omega, T) = B(T)\omega^s \quad (8)$$

here  $B(T)$  is a constant, generally, dependent on temperature, and the frequency exponent  $s$  lying between 0 and 1, can be determined from the linear slope of  $\log\sigma_{ac}$  versus  $\log\omega$ .

### 4. Experimental detail:

Mixture of Polyvinyl alcohol (PVA) with potassium hydrogen sulfate ( $KHSO_4$ ) with different weight ratios of sodium iodide (NaI) (0, 10, 20, and 30 wt%) were prepared by casting method. The electrolyte composites were prepared by dissolving (2 - x)mg PVA, 0.2 gm  $KHSO_4$  and x gm NaI in 25 ml distilled water. In order to prepare homogenous solution, a magnetic stirrer was used for one hour at 400 K for each concentration; later on, the prepared solutions were separately casted in a glass dish with 5 cm diameter. The whole assembly was placed in a dust free chamber to evaporate slowly in air at room temperature for three days period. The thickness of films was in the range of (0.05 - 0.17)mm, it was determined using micrometer within accuracy  $\pm 0.01$ mm.

For performing a good contact in electrical measurement, both sides of each sample of radius 1.5 cm were coated with silver, sandwiched then pressed between the two similar aluminum electrodes, to avoid the parasite capacitance induced by the presence of air interstices at the interfaces between the sample and the electrodes. The whole assembly was placed in a temperature controllable isolated chamber. Chromel-Alumel thermocouple and a digital multimeter with an accuracy of  $\pm 1^\circ C$  were used for measuring the temperature of the studied

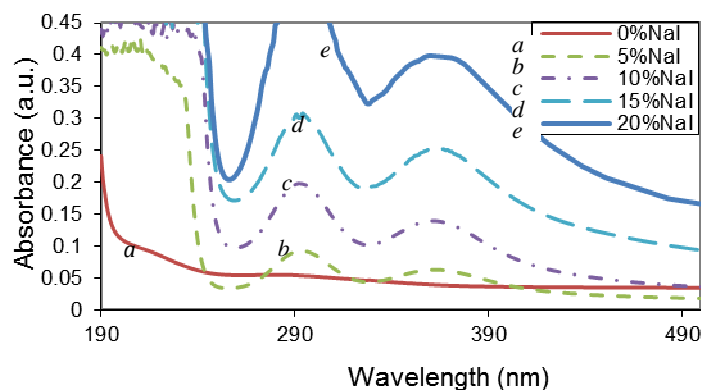
samples.

The absorption spectra of investigated films were recorded at room temperature using UV-VIS double beam spectrometer (Model: Lambda 25), in the wave length range (190 – 1100) nm. The electrical parameters (dielectric permittivity  $\epsilon'$ , dielectric loss  $\epsilon''$  and ac conductivity  $\sigma_{ac}$ ) were calculated from conductance  $G_g$  and capacitance  $C_g$  which were measured using the Programmable Automatic Precision LCR meter type PM6036, in the temperature range (300-350)K over the frequency range from 10 KHz to 1 MHz.

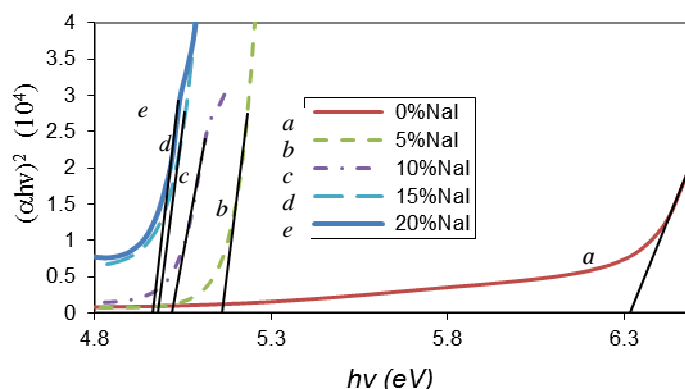
### 5. Results and discussion:

The absorption coefficient spectra for PVA- KHSO<sub>4</sub>-NaI electrolyte composites are shown in Fig.(2). According to the obtained results, two peaks have been observed at nearly (293 and 363) nm in NaI doped samples, the amount of absorbance at each position increase several times with increasing NaI content. The figure indicates that NaI enhances the UV absorption of the PVA host at high concentration. This indicates that PVA- KHSO<sub>4</sub>- NaI electrolyte composites can acts as an excellent ultraviolet shield especially at high NaI content.

Figure (3) shows  $(\alpha h\nu)^2$  versus photon energy  $h\nu$ . The best straight line has been obtained at exponential region, supports the direct allowed electron transition. The optical energy gap  $E_{opt}$  (see Eq.(2)) were calculated from extrapolating of the straight line at the higher energy portion.



Fig(2): The optical absorption coefficient spectrum of PVA-KHSO<sub>4</sub>-NaI electrolyte composites.



Fig(3):  $(\alpha h\nu)^2$  versus photon energy for PVA-KHSO<sub>4</sub>: (0, 5, 10, 15, 20) % NaI contents.

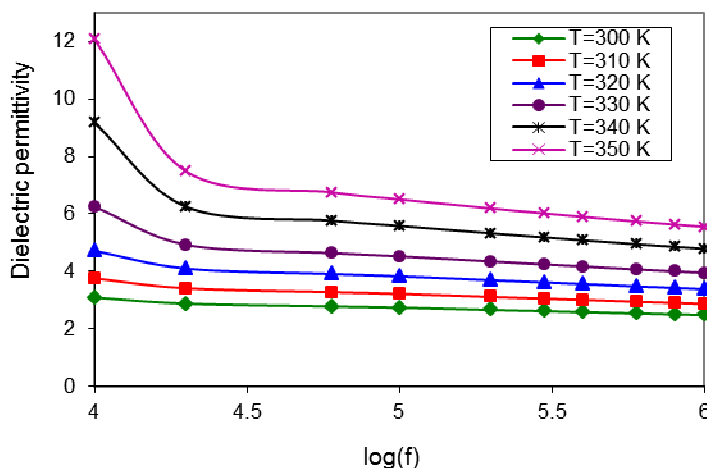
The obtained results show that the optical energy band gap decreased from 6.316 eV (for 0% NaI) to 4.964 eV as NaI concentration increases up to 20 wt% (see Table(1)). These results can be explained in the light of the fact that the increase in NaI content increases the localized states within the forbidden gap, creating band tail, which directly affects the decrease in the optical energy gap of the PVA host.

The decrease in  $E_{opt}$  with increasing salt concentration can be understood by considering the mobility gap variation in the doped polymer [6]. Also the decrements of  $E_{opt}$  may be due to the transition between the molecular orbitals, which have highest occupied molecular orbitals 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 [12].

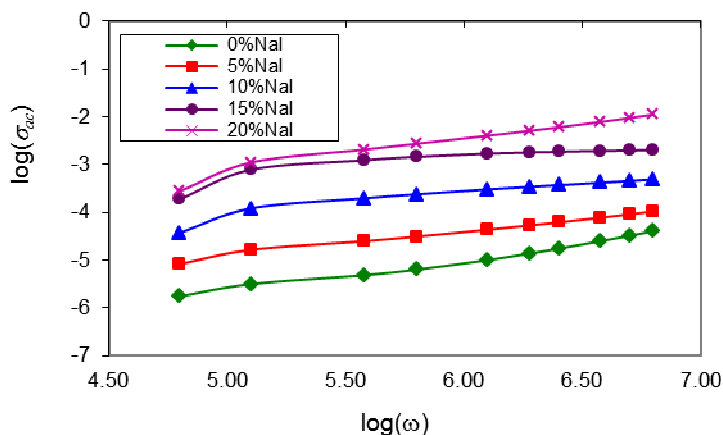
Dielectric measurements were performed in the frequency region **10KHz** to **1MHz**. Fig(4) shows that the dielectric permittivity decreases with increasing frequency for undoped PVA film. The dielectric permittivity of polymer also depends on temperature. As the temperature increases polymer becomes soft and mobility of the main chain segments as well as the rotation of side groups become easier. Thus, as temperature increases the dielectric permittivity increases [18].

The variation of dielectric permittivity with temperature is different for nonpolar and polar polymers. In general, for nonpolar polymers the dielectric permittivity is independent of temperature; but in the case of strong polar polymers the dielectric permittivity increases as the temperature increases [19]. The decrease trend of dielectric permittivity with frequency could be due to the dipoles that not able to follow the field variations at high frequency.



**Fig(4):** Dielectric permittivity of undoped PVA versus  $\log(f)$  at different temperature.

The frequency dependence of the **ac** conductivity  $\sigma_{ac}$  for PVA-KHSO<sub>4</sub>-NaI electrolyte composite films at **350K** is shown in Fig.(5). According to the obtained results,  $\sigma_{ac}$  increases with increasing frequency and NaI content. As the NaI concentration is increased, the NaI molecules start bridging the gap separating the two localized states which facilitating the transfer of charge carrier between two localized state [18]. The variation of the exponential factor **s** was calculated from slope of the Fig.(6), the results are shown in Table(1). The variation of exponent **s** with NaI content gives information on the specific mechanism involved.



**Fig(5):** Logarithmic plot of ac conductivity and angular frequency of PVA-KHSO<sub>4</sub>-NaI at temperature 350 K.

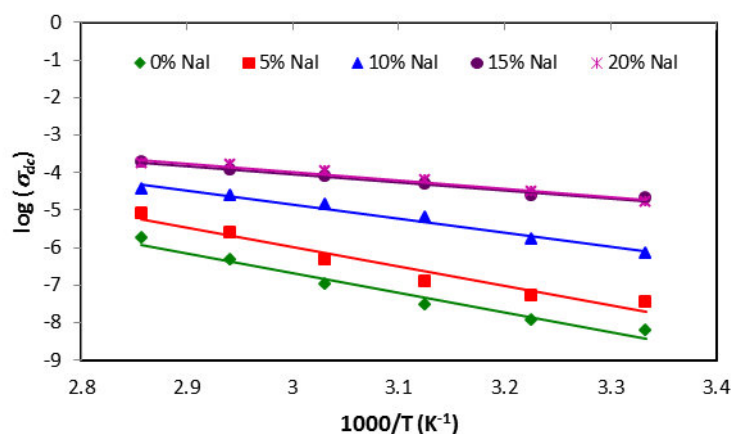
The frequency dependent conductivity is caused by the hopping of the charge carriers in the localized state and also due to the excitation of charge carriers to upper states in the conduction band [20,21]. The conductivity of

polymer also depends on temperature, as the temperature increases polymer becomes soft and mobility of the main chain segments as well as the rotation of side groups become easier. Thus, at higher temperature more and more dipoles are oriented resulting in the higher equivalent surface charge density i.e. as temperature increases conductivity increases follows Arrhenius equation.

The **dc** electrical conductivity  $\sigma_{dc}$  is evaluated from **ac** conductivity data at lower frequency, the temperature dependent of  $\sigma_{dc}$  can be expressed by the Arrhenius equation [20,22]:

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \quad (9)$$

here  $\sigma_0$  can be considered as the limiting value of conductivity at an infinite temperature,  $E_a$  is the activation energy for conduction,  $k$  is Boltzmann constant, and  $T$  absolute temperature. The value activation energy  $E_a$  have been calculated from the slope of the variation of  $\log(\sigma_{dc})$  versus  $(1/T)$  of semi-logarithmic relation of Eq. (9) at different NaI concentrations (see Fig.(6)).



**Fig(6):** Semilogarithmic plots of dc conductivity against reciprocal of temperature at different Carbon black concentrations.

Table(1) shows the values of the activation energy  $E_a$  with NaI concentrations,  $E_a$  have been calculated from the slop of the best-fitted line for each concentrations.

**Table(1):** Variation of the  $E_{opt}$ ,  $s$ , and  $E_a$  with NaI concentration additive to  $(PVA)_{0.9}-(KHSO_4)_{0.1}$ .

NaI%	$E_{opt}$ (eV)	$s$	$E_a$ (eV)
0	6.316	0.722	1.045
5	5.158	0.539	1.028
10	5.023	0.394	0.752
15	4.981	0.321	0.521
20	4.964	0.552	0.448

The calculated results show that the activation energy  $E_a$  decreases with increasing the NaI content. The addition of NaI to PVA-KHSO<sub>4</sub> host enhances the electrical conduction of PVA due to the electronic and impurity contributions arising from NaI and KHSO<sub>4</sub>.

The increase of conductivity at higher temperature could be attributed to high mobility of free charges which makes them more frequency independent; as a result the **dc** conductivity increases with temperature.

## 6. Conclusions:

PVA-KHSO<sub>4</sub>-NaI electrolyte composite films with different concentration sodium iodide have been prepared by casting method. The calculated values of the optical parameters illustrated that there was a reduction in direct allowed optical energy gap values of the films by increasing NaI concentration.

The resent work shows the combined effect of NaI concentration, frequency, and temperature on the electrical behaviour of PVA-KHSO<sub>4</sub>-NaI electrolyte composite. The dielectric permittivity was found to be decrease with increasing frequency and increase with increasing temperature. This behavior was attributed to the polar nature of the PVA. The **ac** conductivity of the electrolyte composite was increases with increasing temperature, frequency, and NaI content.

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