

# Electrical and Dielectric Properties of PVA: CuI Nanocomposites

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## Abstract:

**P**VA/CuI polymer composite samples have been prepared using casting method. PVA/CuI thin films behaves as a n-type and p-type semiconductor. The carrier's concentration and mobility decrease with increase of the CuI concentration. An increase of dc conductivity by increasing CuI concentration is recorded up to 20 wt%, besides it obeys Arrhenius plot with an activation energy in the range 0.54–1.32 eV. The A.C conductivity ( $\sigma_{ac}$ ) have been measured by LCR meter with frequencies range (100-  $2 \times 10^5$ ) Hz and show increases with increasing frequency following the universal dielectric response law. The frequency dependence of ac conductivity showed power law with an exponent  $0.839 < s < 0.998$  which predicts hopping conduction mechanism. The dielectric behaviors of polymer matrix strongly depend on frequency and additive content. The dielectric behaviors such as: dielectric constant ( $\epsilon_1$ ) and dielectric loss ( $\epsilon_2$ ) increases with increase in CuI nanoparticle concentration, but decreases with increase in frequency. The frequency dependence of both dielectric permittivity and dielectric loss obeys Debye dispersion.

**Keyword:** nanocomposite; CuI nanoparticle; activation energy; dielectric constant; dielectric loss, PVA.

## I. INTRODUCTION

A growing interest in the development of ion-conducting polymer electrolytes (ICPEs) have been the main focus of attention because of their potential applications in solid state electrochemical storage and display devices [1 – 5]. Ionic conductivity in polymeric materials was reported by Fenton et al. in 1973 [6] for the first time.

Polymer electrolytes recently have been a subject of great interest due to theoretical interest as well as practical importance for the development of electrochemical devices, such as rechargeable batteries, capacitors and sensors [7]. Further, polymers, on doping with metal nanoparticles, show novel and distinctive properties obtained from the unique combination of the inherent characteristics of polymers and properties of the metal nanoparticles. Over the years, polyvinyl alcohol (PVA) polymers have attracted attention due to their variety of applications. PVA is a potential material having high dielectric strength, good charge storage capacity and dopant-dependent electrical and optical properties. It has carbon chain backbone with hydroxyl groups attached to methane carbons; these OH groups can be a source of hydrogen bonding and hence assist the formation of polymer composite [8-10].

Polymer films such as polyester, polycarbonate, polypropylene, polystyrene, polyethylene sulphide and recently polyvinyl acetal [11] are being used in the fabrication of low leakage capacitors. Though polymers possess relatively low dielectric permittivity, they can withstand high fields, are flexible and easy to process. By combining the advantages of both, one can fabricate new hybrid materials with high dielectric permittivity, and high breakdown voltages achieve high volume efficiency and energy storage density for applications in capacitors as electric energy storage devices [12-19].

The D.C conductivity in semiconductors depends on the presence of free electrons and free positive holes. At (0K), the valance band is regarded as filled and conduction band is empty. As temperature is raised the free electrons are excited into conduction band, and this leaved behind holes in valance band.  $\sigma(\omega)$  dominates at high frequencies or low temperatures while  $\sigma_{dc}$  dominate at low frequencies or high temperatures (The difference between ac and dc conductivity is that they use different models to analyze their data). This means that dc-activation energy is always greater than for ac-conductivity [20].

In the present work, polymer thin films based on PVA doped with CuI has been prepared. The Hall effect measurements are used to measure the carrier concentration and mobility, and it is used to distinguish whether a semiconductor is n or p – type. The temperature dependence (in the temperature range 303–433 K) of electrical conductivity has been studied along with measurement of activation energy. A.C conductivity and the dielectric behaviors such as: dielectric constant ( $\epsilon_1$ ) and dielectric loss ( $\epsilon_2$ ) also have been studies as a function of frequency range (100-  $2 \times 10^5$ ) Hz.

## II. EXPERIMENTAL

The polymer matrix is Poly vinyl alcohol (PVA),  $[C_2H_4O]_n$ , where  $n = 1,60,000$ , chemicals used in the present study were provided by HIMEDA Chemical Company, India. Polymer layers were prepared by the solution cast technique. PVA solution was prepared by adding first distilled water to solid PVA [1g of PVA in 30ml of distilled water] and using magnetic stirrer [at  $90^\circ$  C for 2 h] for the mixing process to obtain more homogeneous solution. CuI particles were added with concentrations (0,1,3,5,7,9 and 20) wt%. By using casting

method, we get the films from this mixture in the template in Petri-glass dishes and on Microscope glass slides (the substrates were first cleaned in ethanol solution, subsequently ultrasonically washed with distilled water) and left for two weeks at room temperature to dry.

Thick layer of polymer electrolyte of thickness between 450 and 550 nm were subjected to conductivity measurements where silver past was used as conducting electrodes on the desired area. The electrical conductivity has been measured as a function of temperature for PVA/CuI films in the range (303 – 433) K. The measurements were done by using sensitive digital electrometer type Keithley (616) and electrical oven. The resistivity ( $\rho$ ) of the films is calculated by using the following equation:

$$\rho = \frac{R \cdot A}{L} \quad \dots\dots\dots(1)$$

where R is the sample resistance, A is the cross section area of the films (A = width of Al electrode x thickness of sample) and L is the distance between two Al electrodes.

The conductivity of the films is determined from the relation:

$$\sigma = \frac{L}{R \cdot A} \quad \dots\dots\dots(2)$$

The D. C. activation energies could be calculated from the plot of  $\ln \sigma_{d.c}$  versus  $1000/T$ . For most cases of semiconductor the following equation gives the change of the electrical conductivity with temperature:

$$\sigma = \sigma_0 \exp(-E_a/K_B T) \quad \dots\dots(3)$$

where:  $\sigma_0$  : is the minimum electrical conductivity at 0 °K,  $E_a$  : is the activation energy which corresponds to ( $E_g/2$ ) for intrinsic conduction, T: is the temperature and  $K_B$  is the Boltzman's constant[20].

The Hall effect measurements are carried out to determine the type, mobility by using Hall effect system (HMS-3000) supplied by the Ecopia company. It has been placed in four point and opposite sides of a thin sheet of conducting or semi-conducting material through which an electric current is flowing, created by a magnetic field ( $B=0.550$  Tesla).

The PVA/CuI film samples were prepared in coplanar configuration between two (Al) thin film electrodes, the samples and Al electrode are deposited onto glass substrate using mask. For ac- measurement, LCR meter model 821, has been used to measure the capacitance (C), resistance (R). The conductivity of the films is determined from the relation in the equation (2). The dielectric constant ( $\epsilon_1$ ), and dielectric loss index ( $\epsilon_2$ ) were recorded at frequency 10 kHz –  $2 \times 10^5$  Hz. Both  $\epsilon_1$  and  $\epsilon_2$  were calculated as follows [21]:

$$\epsilon_1 = \frac{C}{\epsilon_0 A} \quad \dots\dots\dots(4)$$

where (C) is the capacitance of the sample and ( $\epsilon_0$ ) is permittivity of the space ( $8.854 \times 10^{-12}$  F.m<sup>-1</sup>), and

$$\epsilon_2 = \epsilon_1 \cdot \tan \delta \quad \dots\dots\dots(5)$$

The total conductivity  $\sigma_{tot}(\omega)$  at particular frequency is given by

$$\sigma_{tot}(\omega) = \sigma_{dc} + A\omega^s \quad \dots\dots\dots(6)$$

where  $\sigma_{dc}$  is the dc conductivity at zero frequency,  $\omega$  is the angular frequency, s is the frequency exponent and A is frequency independent preexponential factor.

### III. RESULT AND DISCUSSION

#### 1-Hall effect

To investigate the type of charge carriers of the material, concentration and their mobilities, Hall effect measurements for PVA/CuI thin films deposited at room temperature were studied. The sign of Hall coefficient ( $R_H$ ) indicates that PVA/CuI thin films behave as a n-type semiconductor and p-type. The carrier's mobility was calculated from equation.

Table 1 shows the values of Hall Effect measurements, charge carriers, concentration and their mobilities for PVA/CuI films with different CuI concentration. It can be observed from table 1 that the carrier's concentration and mobility decrease with increase of the CuI concentration.

Table 1. values of Hall Effect measurements, charge carriers, concentration and their mobilities for PVA/CuI films with different CuI concentration.

CuI concentration	$R_H$ (cm <sup>2</sup> /c) X10 <sup>7</sup>	$N_H$ (cm <sup>-3</sup> ) x10 <sup>11</sup>	$\sigma_{d.c}$ at R.T (Ωcm) <sup>-1</sup> x10 <sup>-6</sup>	$\mu_H$ (cm <sup>2</sup> /v.sec)	type
0	15.3	7.318	4.144	553.4	P
1	0.417	1.231	2.927	540.3	P
3	-0.279	-1.155	2.333	192.2	N
5	-0.075	-2.645	2.011	130.6	N
7	1.733	0.6872	0.072	2.689	P
9	0.000296	2.785 x10 <sup>11</sup>	0.6276	60.30	P
20	0.2758	2.920	366.8	•	P

#### 2-D.C Conductivity

Figure 1 illustrates temperature dependence of bulk conductivity for different concentrations of CuI (0–20 wt%); they illustrate clearly that the conductivity is thermally activated with increasing temperature and follows the Arrhenius relation.

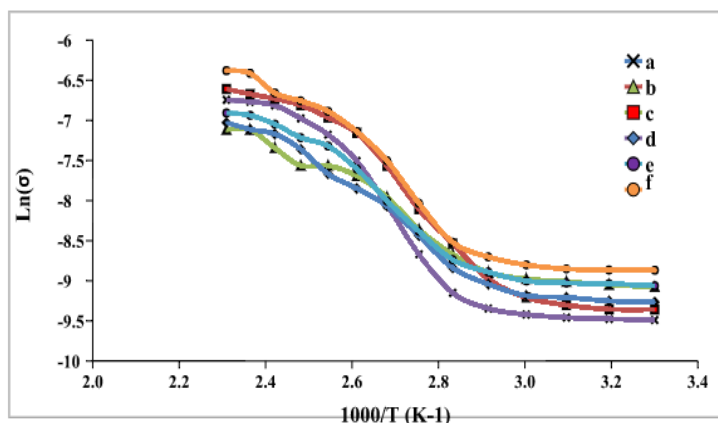


Fig 1. Variation of  $\text{Ln}(\sigma)$  with reciprocal temperature for (PVA/CuI) films with different CuI dopant ratio ( 0, 3, 5,7, 9 and 20) %.

The results illustrate the two regions characterizing conduction at relatively low and high temperature respectively. The values of  $E_a$  are obtained by least square fitting of Eq.(3), and listed in table 2.

Table 2: DC activation energies, their ranges and conductivity at room temperature for (PVA/CuI) thin films at different CuI content.

CuI concentration	Sample	$E_{a1}$ (eV)	Range (K)	$E_{a2}$ (eV)	Range (K)	$\sigma_{RT} (\Omega \cdot \text{cm})^{-1} \times 10^{-5}$
0	a	0.265	303-353	0.629	353-433	7.58
3	b	0.185	303-353	0.295	353-433	11.5
5	c	0.301	303-353	0.472	353-433	8.63
7	d	0.197	303-353	0.376	353-433	9.47
9	e	0.198	303-353	0.311	353-433	11.6
20	f	0.059	303-353	0.346	353-433	14.1

It can be seen from this table that bulk conductivity increases as the increase in the CuI concentration up to 3% then starts to decrease as the concentration of CuI further increases, then again increases as the increase in the CuI concentration. It is clearly observed that  $E_{ac}$  varies irregularly with CuI concentration which can be attributed to the composite structure and salt complexation with polymer matrix. These properties depend on CuI nanoparticles concentration, particle size, dispersion, polymer– nanoparticles interaction (polymer – particle interfaces). These results are in agreement with[22-24].

### 3-A.C Conductivity

The frequency dependence of the total conductivity ( $\sigma_{tot}$ ) for the polymer composites (calculated using equation 6) at 303 K of different concentrations is given in Figure 2 .

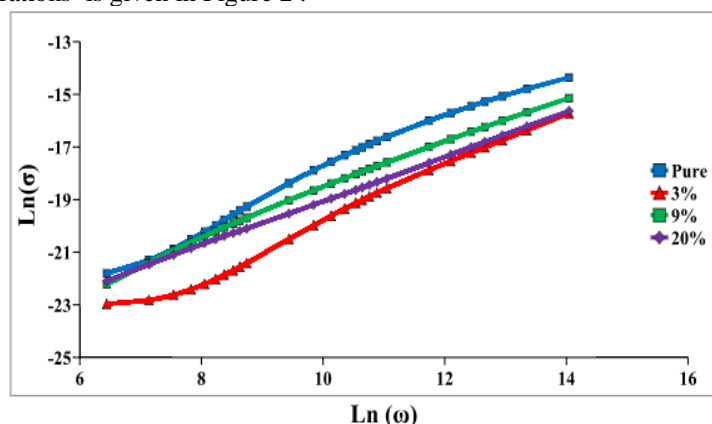


Fig 2. Variation of  $\text{Ln}(\sigma)$  with reciprocal frequency for (PVA/CuI) films with different CuI dopant ratio (0, 3, 9 and 20) %.

The figures show that A.C conductivity increases considerably with the increase of frequency from 100 Hz to  $2 \times 10^5$  Hz. This is attributed to the space charge polarization that occurs at low frequencies and to the motion of charge carriers by hopping process. The conductivity is increases with the increasing of the concentration because of the increase of the charge carriers and the formation of a continuous network of (CuI) inside the (PVA/CuI) polymer composite. The

increases of the conductivity is small at high frequencies; this is attributed to the electronic polarization and the charge carriers, which travel by hopping process [25]. Consequently, the conductivity is increasing when the frequency increases for all different rates of the concentration.

The strong frequency dependence of ac conductivity can be described by the second term in equation 6. However, the values of the exponent  $s$  have been obtained using the least square fitting which lie in the range  $0.839 < s < 0.998$ ; these values predict hopping conduction in the CuI/PVA composites under investigation.

#### 4- Dielectric Constant

Figure 3 illustrates the effect of adding CuI on the dielectric constant at temperature of  $30^\circ\text{C}$ . Decrease dielectric constant with increasing concentration of CuI can be explained due to continuous network of CuI inside composite polymer (PVA / CuI). These results are in agreement with [26].

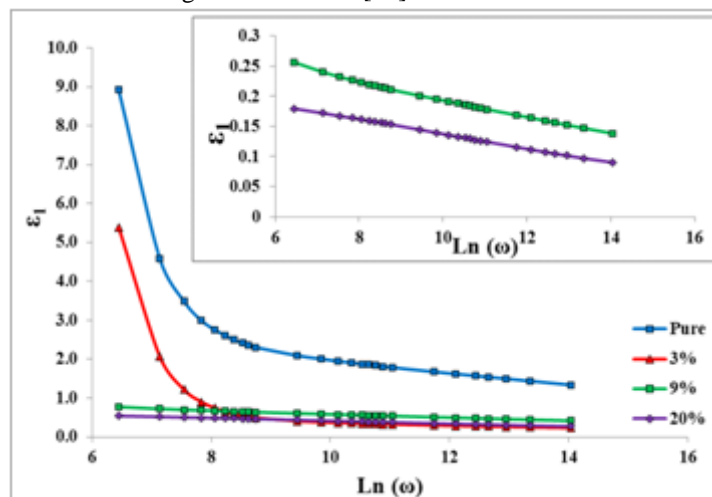


Fig 3. Frequency dependence of the ( $\epsilon_1$ ) of the dielectric constant for PVA/CuI thin films with different CuI concentration

Figure 3. note dielectric constant value decreases with the increase in frequencies. The decrease of dielectric constant ( $\epsilon_1$ ) with frequency can be associated to the inability of dipoles to rotate rapidly leading to a lag between frequency of oscillating dipole and that of applied field. The variation indicates that at low frequencies the dielectric constant is high due to the interfacial polarization and the dielectric loss ( $\epsilon_2$ ) becomes very large at lower frequencies due to free charge motion within the material [19]. These results are in agreement with [26,27]. The increase of frequencies results in decreasing of space charge polarization (interfacial polarization) to the total polarization. The space charge polarization becomes the more contributing type of polarization at low frequencies, and less contributing with the increase of frequency; this would result in the decrease of dielectric constant values for all samples with the increase of the electric field frequency ( $f$ ). Moreover, PVA exhibits flexible polar side groups with a polar bond as the bond rotating having intense dielectric transition [28].

The other types of polarizations appear at high frequencies, the ionic polarization reacts slightly to the variation in the field frequencies compared to the electronic polarization. This is because the mass of ion is greater than that of the electron. The electrons respond to even the high frequencies of the field vibrations. The low mass of electron makes the electronic polarization, the only type of polarization at higher frequencies. This makes the dielectric constant approximately constant for all samples at high frequencies.

#### 5- Dielectric Loss

Figure 4 Show the dielectric loss of (PVA/CuI) nanocomposites as a function of frequency .

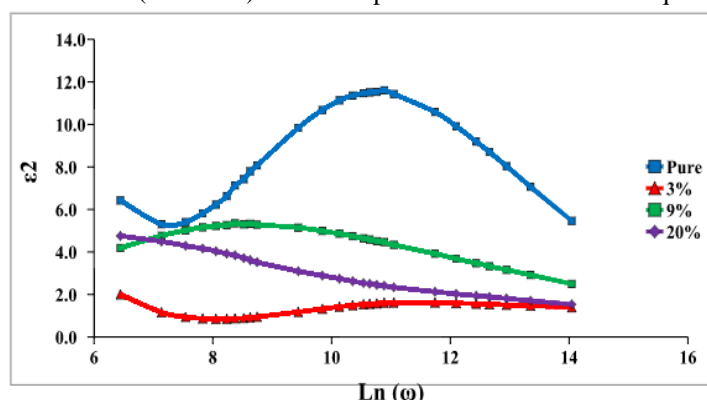


Fig 4. Frequency dependence of the ( $\epsilon_2$ ) of the dielectric loss for PVA/CuI thin films with different CuI concentration

When the applied field frequency is low, the dielectric loss value is high, and it decreases when the frequency increases. This is attributed to the decrease of the space charge polarization (interfacial polarization) contributes when the frequency increases. The dielectric loss increases again until it reaches to the highest value at ( $f=100$  Hz) When the frequency ( $f$ ) is increases to 6 kHz, the dielectric loss is approximately constant, . The value of dielectric loss increases by increasing the concentration of (CuI) ; this is due to the increase of the charge carriers caused by the increase of the (CuI) concentration. These results are in agreement with[26,29].

#### IV. CONCLUSIONS

Different compositions of PVA: CuI polymer electrolyte samples have been prepared by solution cast technique. It is found that addition of CuI salt increases conductivity. The high electrical conductivity is achieved due to increasing number of free ions after dissociation of salt. The temperature dependent conductivity plot shows two distinct Arrhenius type behaviors. The minimum activation energy 0.059 eV is observed for PVA-20 % CuI system. The A.C electrical conductivity for all concentrations increases with the increasing of the frequency of the applied electrical field, while the dielectric constant and dielectric loss of the (PVA/CuI) nanocomposites are decreasing with the increasing of the frequency .

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