

## Study of electrical conduction mechanism of (0.2%) Polyaniline doped PVC-PVAc polymer blends

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### Abstract:

The electrical conduction of polyaniline doped polyvinylchloride (PVC) and polyvinyl acetate (PVAc) thin films has been measured by studying the I-V characteristics at various temperature in the range 323-403 K. The results are presented in the form of I-V characteristics and analysis has been made by interpretation of Poole-Frenkel, Fowler-Noodheim, Schottkyln ( $J$ ) vs  $T$  plots, Richardson and Arrhenius plots. The results analyzed suggests that schottky and Richardson mechanisms are primarily responsible for the observed conduction.

**Keywords :** Polyaniline doped PVC-PVAc polymer blends: PACS No. : Conductivity 72.20-1, 73.69 Ph

### Introduction:

Electrical properties constitute one of the most convenient and sensitive method for studying the polymer structure<sup>1</sup>. In recent years polymer composites have steadily gained growing importance. A good amount of work has been reported on the electrical conduction mechanism in polymeric materials. The electrical conduction in polymer film has much importance due to the discovery of the memory phenomenon<sup>2</sup> and has wide application now-a-days in thin film devices<sup>3</sup>. In the present years, because of the need for electrostatic charges dissipation, electromagnetic shielding etc, new polymers with electrical conductivity have been formulated. This led to new discoveries in the area of conducting polymers, which has now become one of the hot topics of research<sup>4</sup>.

Mishra et al<sup>5</sup> measured the dc-electrical conductivity of glycine to study the mechanism of electrical conduction and results are analysed in terms of Schottky-Richardson mechanism which is primarily, responsible for the conduction. The electrical conduction in iodine-doped polystyrene (PS) and polymethyl methacrylate (PMMA) have already been reported<sup>6,7</sup> Belsare et al<sup>8</sup> have reported the electrical conductivity of iodine-doped polyblend films of polystyrene (PS) and polymethyl methacrylate (PMMA).

Japanese scientists<sup>9</sup> have been particularly active in early research and development of these devices with work on natural and synthetic polymers. Most of the early polymer electrets work in the U.S. have been focused on using the piezoelectric response for electromagnetic radiation detection<sup>10,11</sup>.

Burghate<sup>12</sup> have reported the electrical conduction mechanism of succinic acid (6%) doped glycine (94%) pellet. Deshmukh et al<sup>13</sup> reported electrical conduction in semiconducting PVC-PMMA thin film. Segal et al<sup>14</sup> have reported Polyaniline / PVAc blends : Variation with time of structure and conductivity of films cast from aqueous dispersions. The electric conductive composites based on core shell Polyaniline nanoclay by latex blending have been reported by Yingfeng et al<sup>15</sup>.

In the case of organic solid where the conductivity due to electrons excited from valence band to conduction band<sup>16,17</sup> is negligible, a complex conduction behavior<sup>17,18</sup> has been explained usually in terms of electron emission from cathode i.e. Schottky-Richardson mechanism<sup>19</sup> or by electron liberation from the traps in the bulk of the material i.e. Poole-Frenkel mechanism<sup>20</sup>. However possibility of tunneling<sup>21</sup>, space charge limited conduction<sup>22</sup> etc. have also been discussed in the literature.

Conjugated Conducting polymers such as Polypyrrole (PPY), Polyaniline (PANI), Polythiophene (PT) and so forth are the most interesting conducting polymers due to their excellent chemical and electrochemical stability. They are easy to prepare in the form of large area thin films and are capable of storing charge throughout their entire volume. Conjugated polymers, most notably polyaniline (PANI), polypyrrole (PPY), polythiophene (PT), poly(3,4-ethylenedioxythiophene) (PEDOT), and poly



(p-phenylenevinylene) (PPV) have been synthesized, in free-standing film and bulky powder forms, using electrochemical or chemical polymerization methods. PANI can be formed chemically or electrochemically through oxidative polymerization of aniline monomers, the final form of PPY and PANi are those of a long conjugated backbone.<sup>23</sup>

In the present study, d. c. conduction of donor-acceptor mixed polymers doped with polyaniline was measured to identify the mechanism of electrical conduction. It shows how the I-V-data of the sample can be used to arrive at a possible conduction. Results have been discussed by plotting different mechanisms, such as Poole - Frenkel, Fower - Nordheim, log (J) versus T plots, Schottky plots, Richardson plots. In case of Schottky - Richardson mechanism the current shows strong temperature dependence but not in case of Poole - Frenkel mechanism. The study of temperature dependence of current density is, therefore, of great importance. The X-ray diffractogram (XRD) shows that the crystallinity is almost negligible showing the sample is amorphous.

## Experimental details:

### 2.1 Preparation of Samples

The polyvinylchloride (PVC) of standard grade product supplied by polychem Industries, Mumbai and (PVAc) of standard grade were used for the study. The two polymers PVC (1.2 g) and PVAc (0.3 g) were taken in the ratio of 4:1 by weight and PANI of weight 0.003g i.e. 0.2%. The 1.2g PVC in 15 ml of tetrahydrofuran (THF), 0.3g PVAc in 10ml of tetrahydrofuran and PANI in 5ml of THF were dissolved separately. After allowing them to dissolve completely, all the three solutions were mixed together. The solution was heated at 60<sup>0</sup>C for two hours to allow polymers to dissolve completely to yield clear solution. A glass plate (15 cm X 15cm) thoroughly cleaned with hot water and then with acetone was used as a substrate.

To achieve perfect leveling and uniformity in the thickness of the film, a pool of mercury was used in the plastic tray in which the glass plate was freely suspended. The whole assembly was placed in a dust free chamber maintained at constant temperature (40<sup>0</sup>C). In this way the film was prepared by isothermal evaporation technique<sup>24,25</sup>. The film was subjected to 12 hrs heating at constant temperature 50<sup>0</sup>C and kept for another 12 hrs at room temperature to remove the traces of solvent. Finally, the film was removed from the glass plate. It was cut into small pieces of suitable size, which were washed with ethyl alcohol to remove the surface impurities. The X-ray powder diffractogram of sample, recorded from a Philips (Holland) automated diffractometer (RSIC-Nagpur) is shown in Fig 1. The absence of peak in the X-ray spectra confirmed the amorphous nature of polymer sample.

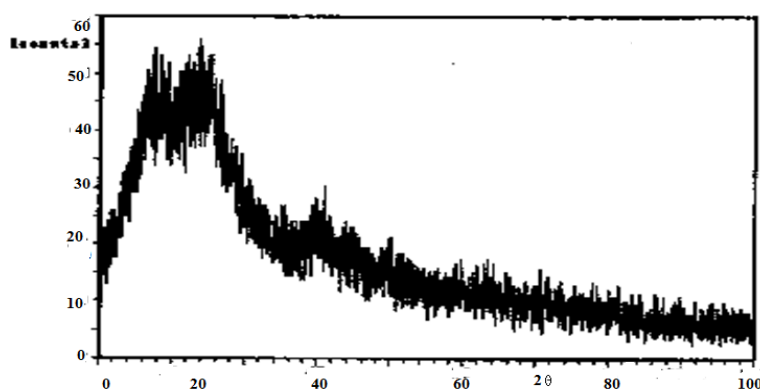


Fig 1 : X-ray diffractogram

### 2.2 Thickness Measurements:

For measuring the thickness micrometer screw gauge<sup>26</sup> least count 0.001cm (10 μm) was used. But for greater accuracy and resolution, a compound microscope in conjunction with an acculometer which

gives least count 13  $\mu\text{m}$  and 3.3  $\mu\text{m}$  at the magnification of 1:10 and 1:100 respectively, was used. A small section of the sample was taken and mounted vertically to get a clear section view of the thickness. The film used for the present study is of thickness 60 $\mu\text{m}$ .

### 2.3 Electrode coating:

The electrode coating on the film of measured thickness was done by using the <sup>(27, 25)</sup> quick drying and highly conducting silver paste supplied by eltecks corporation, Bangalore. A mask of a circular aperture 2-5cm diameter was used while coating, to ensure uniformly in size of coated silver electrode.

### 2.4 Measurements:

For the measurement of current and voltages, the thermostatically controlled furnace supplied by Tempo Industrial Corporation, Mumbai, was used for heating purpose. The mercury thermometer with an accuracy  $\pm 1^\circ\text{C}$  was used to record the temperatures. The regulated power supply supplied by Nupur India was used as the voltage source, while the current was recorded by using highly sensitive Pico-Ammeter (Model DPA 111 with accuracy  $\pm 0.2\%$  supplied by scientific equipments, Roorkee). The sample film coated with silver electrodes was sandwiched between two brass electrodes (diameter 2.4 cm) of the sample holder specially fabricated in the laboratory. This formed the metal-insulator-metal (M-I-M) system, which was placed in the furnace. The current (I) – voltage (V) measurements have been done at various constant temperatures from 323 to 403 K.

## Results and discussion:

The log (I)-log (V) plots of polyaniline (PANI) doped PVC-PVAc polymer composite at temperatures 323k, 333k, 343k, 353k, 363k, 373K, 383k, 393K 403k are shown in Figure 2

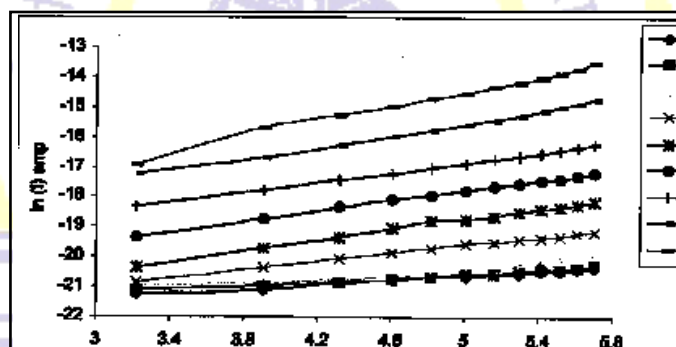


Fig. 2 Current-voltage characteristics

The current increases nonlinearly with the applied voltage and does not follow power law  $I=kV^m$ , where k and m are constant. The possibility of ohmic conduction as well as space charge limited conduction is ruled out from the observed behavior of I-V characteristics. The current in the beginning at low values of voltages increases slowly while it increases at a faster rate at higher values of voltages. Observations similar to these were reported by Mishra and Nath<sup>5</sup>. Fig 2 indicates that (i) the current at a constant temperature increases with applied voltage (ii) the current at constant applied voltage, increases with temperature. The mechanism operative in present case is discussed in the light of the Poole-Frenkel, Fowler-Nordheim, Schottky, log(J) versus T plots, Richardson and Arrhenius plots.

### 3.1 Poole-Frenkel mechanism:

The current-voltage relationship for Poole-Frenkel mechanism<sup>20</sup> is expressed as

$$J = B \exp\left(\frac{-\varphi}{kT} + \beta_{PF} E^{1/2}\right)$$

where  $\beta_{PF} = \left[\frac{e}{kT} \left(\frac{e}{\pi \epsilon \epsilon_0 d}\right)\right]^{1/2} = \text{constant}$  ----- (1)

Where  $\beta$  is a constant and all other symbols have their usual meanings. The Poole-Frenkel mechanism predicts a field dependent conductivity as

$$\sigma = \sigma_0 \exp\left(\frac{\beta_{PF} E^{1/2}}{2kT}\right) \quad \text{-----(2)}$$

$$\text{Or } \ln \sigma = \ln \sigma_0 + \frac{\beta_{PF} E^{1/2}}{2kT} \quad \text{-----(3)}$$

So that the Poole-Frenkel mechanism is characterized by the linearity of  $\log \sigma$  versus  $E^{1/2}$  plots i.e. Poole-Frenkel Plots predicted by eqn (3) are linear with +ve slope (Fig 3).

In the present case of PANI doped PVC-PVAc polymer composite the  $\log \sigma$  versus  $E^{1/2}$  plots are linear but with a -ve slope indicating the absence of PF mechanism.

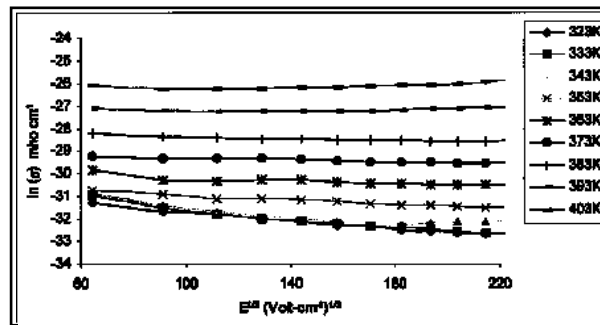


Fig. 3 Poole-Frenkel plots

**3.1 Fowler-Nordheim Mechanism:**

The Fowler-Nordheim relation<sup>21</sup> for current density is :

$$J = AV^2 \exp\left(\frac{-\phi}{V}\right)$$

So that

$$\log \left(\frac{J}{V^2}\right) = \log A - \left(\frac{\phi}{V}\right)$$

And the  $\log J/V^2$  versus  $I/V$  plot is expected to be a linear relation with -Ve slope.

In this case the  $\log J/V^2$  versus  $I/V$  plot for the sample is presented in Fig 4, Which are nearly straight line with a +Ve slope for higher as well as lower values of  $V$  (and of course  $E$ ) indicating the absence of F-N mechanism in all the samples.

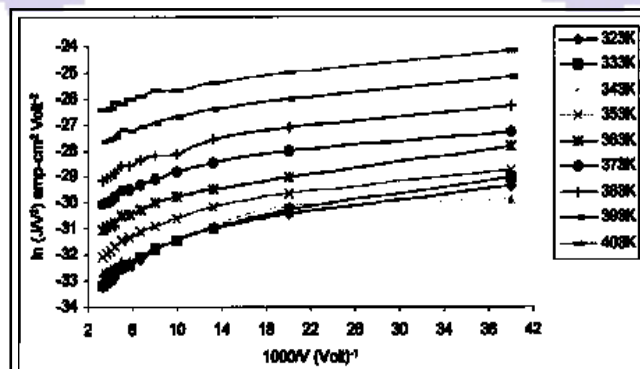


Fig 4 :Fowler-Nordheim plots

**3.2 Schottky plots**

Thermal activation of electron, may occur over the metal insulator interface barrier, which is further helped by the applied electric field effect, which reduces the height of the barrier. The Schottky-Richardson current voltage relationship is expressed as

$$J = AT^2 \exp\left(\frac{\phi_s}{kT} + \beta_{SR} E^{1/2}\right)$$

$$\beta_{SR} = \frac{e}{kT} \left(\frac{e}{4\pi\epsilon\epsilon_0 d}\right)^{1/2}$$

and hence

$$\ln J = \ln AT^2 - \frac{\phi_s}{kT} + \beta_{SR} E^{1/2}$$

and that log J versus  $\sqrt{E}$  plot should be a straight line with a +ve slope.

Schottky-plots for the present case are shown in Fig 5. The relation expects a +ve slope, which is observed in the present case, and such indicates the applicability of the mechanism. Further, in the case of Schottky-Richardson mechanism the current shows strong temperature dependence but not in case of the Poole-Frenkel mechanism. The study of temperature dependence of current density is, therefore, of great importance.

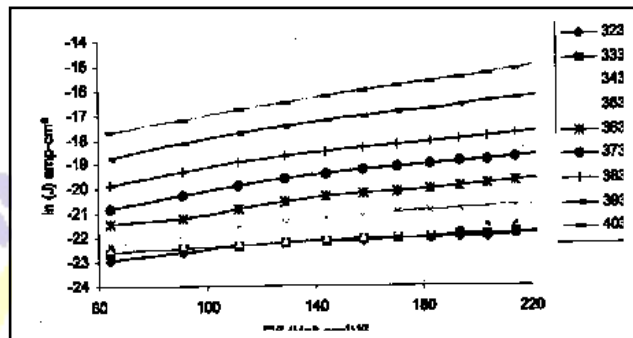


Fig 5 :Schottky plots

### 3.3 Current density versus temperature plots:

The temperature dependence of current density is presented in the form of log (J) versus temperature plots in Fig 6, which shows that log (J) increases linearly with temperature. The strong temperature dependence is in agreement with the Schottky-Richardson mechanism. Further, the straight line with constant slope are observed for all the fields indicating the absence of any thermodynamic transition in the temperature range studied.

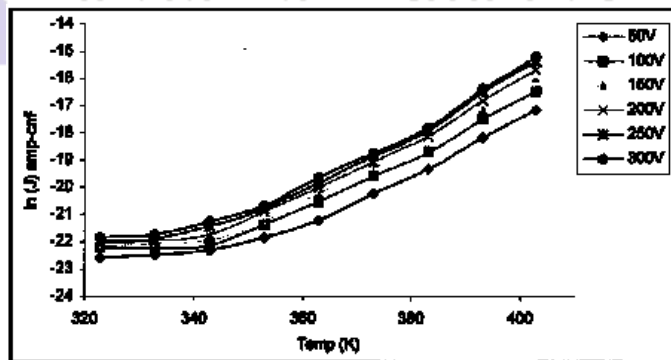


Fig 6 : Current density versus temperature plots

### 3.4 Richardson mechanism

The Richardson current voltage relationship is expressed as,

$$J = AT^2 \exp\left(-\frac{\phi_s}{kT} + \beta_{SR} E^{1/2}\right)$$

$$\frac{J}{T^2} = A \exp \left( -\frac{\phi_s}{kT} + \beta_{SR} E^{1/2} \right)$$

Where  $s$  is metal-insulator potential barrier.

$$\log \frac{J}{T^2} = \log A + \left( -\frac{\phi_s}{kT} + \beta_{SR} E^{1/2} \right)$$

$$\log \frac{J}{T^2} = \log A + \beta_{SR} E^{1/2} - \frac{\phi_s}{kT}$$

The graph between  $\log (J/T^2)$  versus  $(1/kT)$  from this relation should be a straight line with a negative slope.

In the present case such straight line graphs have been obtained with a -ve slope. The linearity of the plots support Schottky-Richardson mechanism.

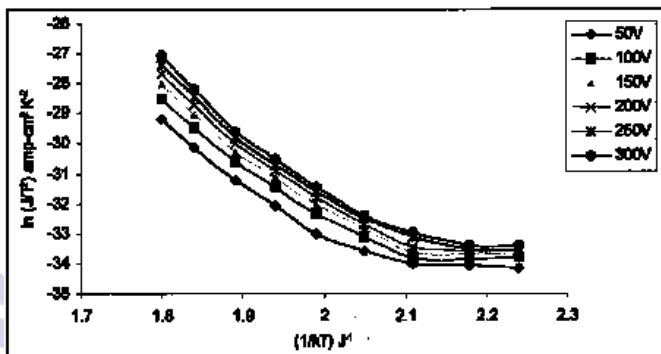


Fig 7 : Richardson plots

### 3.5 Arrhenius Plots

The temperature dependence of conductivity of polyaniline doped PVC-PVAc thin film was presented in the form of Arrhenius plots. The  $\log \sigma$  versus  $1/T$  plots (Fig 8) at all values of applied voltages show parallel straight line with a -ve slope. From the slope of straight line, the activation energy is calculated and is found to be in the neighbourhood of 0.46 eV for LTR and 0.54 eV for HTR. This is in good agreement with the reported order of magnitudes.

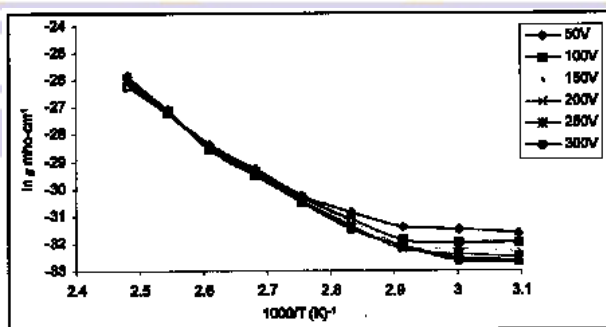


Fig 8 : Arrhenius plots

### Conclusion:

After studying electrical conduction through film under various existing mechanisms, it is observed that in the present case, the behavior can not be described by P-F, F-N mechanism but can be closely described by Schottky and Richardson mechanisms. This is also evident from Arrhenius plots which give activation energy of 0.46eV which lies in the semiconductor range. This is the case with present sample. It seems to be quite interesting to study the conduction mechanism with addition of dopants which are likely to cause changes in the behaviors of the sample and is being undertaken shortly.

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