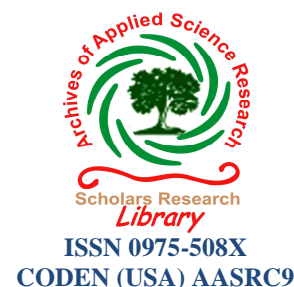




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## Preparation and electrical characterization of free standing PVA-PPy-FeCl<sub>3</sub> composite polymer films

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### ABSTRACT

Polyvinyl alcohol-Polypyrrole composite films were prepared by solution casting technique using chemical oxidative polymerization of pyrrole. Ferric Chloride (FeCl<sub>3</sub>) was used as an oxidizing agent. This technique produces conductive, flexible and free standing polymer composite films. The dc conductivity was obtained from current-voltage characteristics by using two probe technique in the temperature range of 303K -343K. The conductivity increases as temperature and oxidant concentration are increased. The temperature dependence of conductivity is explained using two different models namely Arrhenius and Mott's Variable Range Hopping (VRH) model. Activation energy ( $E_a$ ) and hopping parameters are determined.

**Keywords:** PVA-PPy composite films, I-V characteristics, Conductivity, Arrhenius Model, Mott's equations.

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### INTRODUCTION

The discovery of conductive polymers is unique in its accomplishment as a possible substitute for metallic conductors and semiconductors. [1]. Intrinsically conducting polymers such as polyaniline, poly(*p*-phenylene), polypyrrole and polythiophene have been studied intensively during the last three decades [2]. Among the conductive electroactive polymers, polypyrrole (PPy) has attracted special interest because of some unique chemical and electrochemical properties. PPy is an attractive conducting polymer because of its high conductivity, flexibility in preparation, its stability and good mechanical properties [3]. A wide range of applications have been proposed for polypyrrole like, low ppm detection for toxic gases such as hydrogen sulfide [4], ammonia [5] and nitrogen dioxide [6], as radar absorbing materials [7], for removal of heavy metals [8], for corrosion protection [9], in lithium/polypyrrole batteries [10], actuators [11], super capacitor [12], Protein transport and separation [13].

Although PPy has promising properties and strong criteria to replace metal, it also has drawbacks such as insolubility in common solvents and infusibility up to the decomposition temperature, put limits on its technological applications [3]. Improvement of the structural and electrical properties, can be achieved by forming PPy composites with commercially available polymers or inorganic materials.

The combination of conventional polymers with conductive polymers is an important alternative to obtain new polymeric materials with improved processability, flexibility and controllable conductivity. In such blends, the insulating polymer provides good mechanical properties and processability while the conducting polymer would provide electrical conductivity. Composites of conducting PPy prepared by electrochemical and chemical methods

with other insulating polymers like Poly (vinylacetate) [3], polyvinylidene fluoride (PVDF) [13], polyvinyl alcohol [14], polyvinylchloride [15] polyurethane [16], are reported in the literature.

The aim of present work is to synthesize free standing flexible PVA-PPy-FeCl<sub>3</sub> composite polymer films with good electrical conductivity. The films are prepared by solution casting technique using chemical oxidative polymerization of pyrrole. We have studied dc conductivity behaviour of the films, as a function of temperature with various dopant concentrations. The temperature dependence of conductivity is explained using two different models namely thermally activated model and Variable Range Hopping (VRH) model. Activation energy (E<sub>a</sub>) and hopping parameters, density of states at Fermi level ( $N(E_F)$ ), hopping distance (R) and average hopping energy (W) are determined.

## MATERIALS AND METHODS

### Materials:

The monomer pyrrole was procured from Spectrochem Pvt. Ltd. Mumbai (India). Pyrrole was double distilled at 131°C and stored at 4°C prior to use for synthesis. Polyvinyl alcohol (PVA) was obtained from S. D. Fine Chem. Ltd., Mumbai. Degree of hydrolysis of this powder is 86-89 % and M.W. was 85000 – 124000. It was used as host polymer during the preparation of composites of polypyrrole. Ferric Chloride anhydrous (Iron (III) chloride) was also obtained from S. D. Fine Chem. Ltd., Mumbai. It was used as oxidizing agent during polymerization.

The purity of all chemicals was of analytical grade and used as-received, without further purification (except monomer). All solutions were prepared using distilled water.

### Synthesis of Films:

In this method, a 4% weight to volume polyvinyl alcohol solution was prepared by dissolving PVA powder in distilled water. This was then stirred vigorously at 70°C for 3 hours on a magnetic stirrer with hot plate so as to obtain clear PVA solution, which was then left to cool to room temperature. Next, to this PVA solution, double distilled pyrrole was added in different volume to weight proportions with respect to PVA and stirred vigorously for about 30 minutes. This solution was then cooled to 0-5°C. Polymerization of pyrrole was carried out using Ferric Chloride as the oxidizing agent. The oxidizing agent (in terms of different proportions) was first dissolved in 10 ml of distilled water and then added drop wise to the PVA + pyrrole mixture. This composite solution was gently stirred for 5 hours. A homogeneous black colored solution was obtained. Films of this solution were prepared by pouring a certain small portion on to a flat glass Petri dish or polypropylene surface. The thickness of the film was controlled by the volume of the solution added. Every time 5 ml of the stock solution was poured on to the Petri dish so that the film thickness of approximately 38 to 40 micrometers could be produced. The solvent got evaporated on its own when left to dry at room temperature. Black colored composite films were thus obtained. All the films were stored in a vacuum desiccator for further investigation.

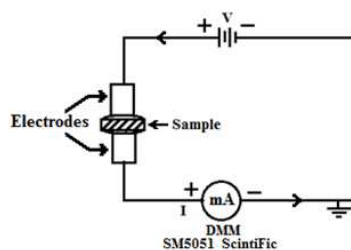
The polymerization of pyrrole occurs on the PVA-transition-metal salt film according to the reaction [17]



### Electrical Characterization:



(a)



(b)

Figure 1. (a) Two Probe Conductivity Measurement System (b) Electrical Circuit Diagram

The apparatus used for conductivity measurement using two probes was specially fabricated in our laboratory shown in Figure 1(a). The electrical circuit diagram is shown in Figure 1(b). This system consists of a sample holder made of two copper electrodes with circular cross section ( $1\text{cm}^2$ ) mounted on a Teflon base provided with a circular screw for applying the required pressure on the sample (film). There was a special arrangement for increasing the temperature of the sample using tiny heater elements. A thermocouple along with an automatic temperature control device helped to measure the temperature over a wide range of  $-100^\circ\text{C}$  to  $+200^\circ\text{C}$ , on a digital display unit. A variable DC voltage up to 5 volts (Navcord) was used to apply the voltage to the PVA-PPy composite films. The current through the sample was measured with the help of a programmable D.M.M. (SM-5015 Scientific). The contact area for the sample was  $1\text{cm}^2$  with the copper electrodes. The films were directly placed between the electrodes for studying the variation of current  $I$  with voltage  $V$ . Further electrical conductivity was measured using the following formula:

$$\sigma = \frac{I}{V} \times \frac{t}{A} \quad (1)$$

Where  $\sigma$  = conductivity in S/cm;  $I/V$  = slope obtained from the  $I-V$  plot.  
 $t$  = thickness in cm;  $A$  = area in  $\text{cm}^2$ ;  $I$  = current in ampere;  $V$  = voltage in volts.

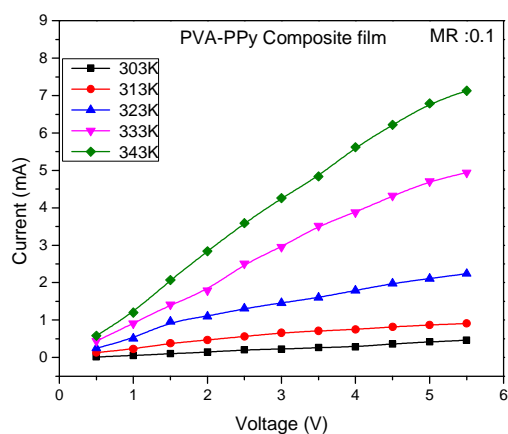
The thickness of the films was measured at five randomly selected places with digital micrometer

The average thickness of the film was found  $40 \pm 2 \mu\text{m}$  for all samples. The measurements were made in the temperature range of 303K - 343K.

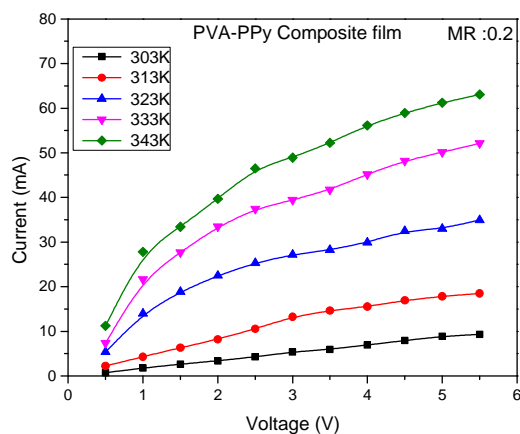
## RESULTS AND DISCUSSION

The electrical conductivity of PPy is the most important property for practical applications. The extended p-conjugated backbone structure of PPy provide electrical conductivity. However, the p-conjugated backbone structure is not sufficient to produce appreciable conductivity. Partial charge extraction from PPy chain is also required, which is achieved by a chemical process called as doping. The conductivity of the neutral PPy is changed from an insulating to a metallic region by doping. It has been reported that the electronic and band structures of PPy change with the doping level [18]. Doping of these polymers creates additional bands in the energy gap, making it possible for the electrons to move to these new bands and increasing the conductivity of the materials [19].

### I-V Characteristics



(a)



(b)

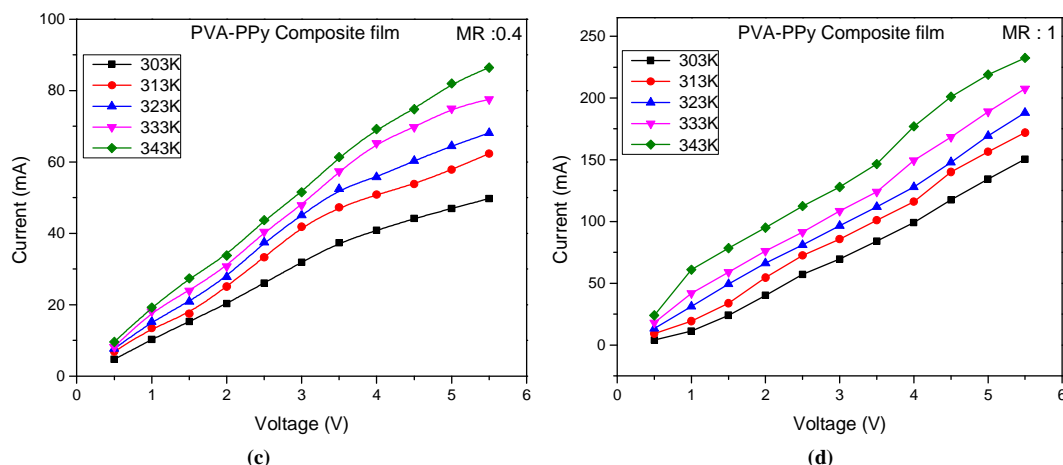


Figure 2. I-V Characteristics of PPy – PVA composite films at different temperatures and MR (a) MR: 0.1 (b) MR: 0.2 (c)MR: 0.8 (d)MR: 1

I-V characteristics of PPy-PVA composite films for four different molar concentrations of oxidant to monomer are shown in Figure 2(a), (b), (c) (d). Each graph has been plotted for five different temperatures. Nearly linear relationship of the I-V curve was observed.

The conductivity of the composite films were estimated using equation (1) and the values obtained are shown in Table 1. It was observed that the electrical conductivity of polypyrrole increased when dopant concentration was increased. It was also observed that the electrical conductivity increased gradually for all the films as the temperatures increased the conductivity also increased with increase in temperature that indicated the semiconducting behavior. For molar ratio more than 1, the films get over oxidized and become brittle.

Table 1. Electrical conductivity of PVA-PPy composite films at different temperatures

Temperature	Electrical conductivity of PVA-PPy composite films (S/cm)			
	MR : 0.1	MR : 0.2	MR : 0.4	MR : 1
303 <sup>o</sup> K	$0.63108 \times 10^{-5}$	$1.25672 \times 10^{-4}$	$6.68814 \times 10^{-4}$	$2.16 \times 10^{-3}$
313 <sup>o</sup> K	$1.11139 \times 10^{-5}$	$2.43557 \times 10^{-4}$	$8.23366 \times 10^{-4}$	$2.399106 \times 10^{-3}$
323 <sup>o</sup> K	$2.75954 \times 10^{-5}$	$3.69976 \times 10^{-4}$	$9.01218 \times 10^{-4}$	$2.457229 \times 10^{-3}$
333 <sup>o</sup> K	$6.75756 \times 10^{-5}$	$5.59243 \times 10^{-4}$	$10.44629 \times 10^{-4}$	$2.675323 \times 10^{-3}$
343 <sup>o</sup> K	$9.7357 \times 10^{-5}$	$6.65058 \times 10^{-4}$	$11.33333 \times 10^{-4}$	$2.932363 \times 10^{-3}$

The variation of conductivity ( $\sigma$ ) with dopant concentration (various molar ratio, MR) at different temperature is shown in Figure 3(a). It is evident from Figure 3(a) that with increase in MR (concentration of  $\text{FeCl}_3$ ) conductivity of these films increases. It shows the conductivity change from  $0.63108 \times 10^{-5}$  S/cm to  $2.16 \times 10^{-3}$  S/cm. This mechanism of conduction is supposed to be by polarons and bipolarons formation due to the dopant molecules [20]. Plots of conductivity ( $\sigma$ ) as functions of temperatures ranging from 303-343K are shown in Figure 3(b). It is evident from Figure 3(b) that with increase in temperature conductivity of these films increases gradually. It shows the conductivity change from  $0.63108 \times 10^{-5}$  S/cm at 303K to  $9.7357 \times 10^{-5}$  S/cm at 343K. In the PPy chain, amino groups in the pyrrole rings donate its lone pair of electron to the aromatic network of the polymer and make themselves electron deficient. When  $\text{FeCl}_3$  was added into the polymer, it formed a donor-acceptor complex in the conjugated system. As a result, quasi-particles were created apparently polarons (cation) and act as charge carriers. At low dopant concentration the polarons have low mobility and exhibit low conductivity. When the polymerization proceeds with increased doping level, more  $\text{Cl}^-$  is bound to the pyrrole ring in the backbone of the polymer chain. At this point, many polarons are created and become crowded to have enough energy to form bipolarons (di-cation). This increases the mobility of the charge carriers which causes the increase in conductivity [21].

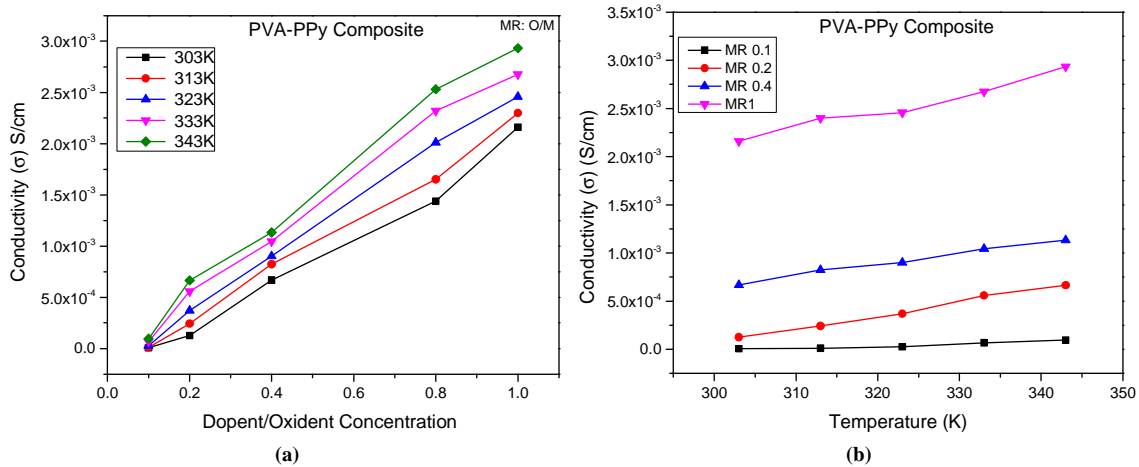


Figure 3. Plots of conductivity ( $\sigma$ ) as functions of (a) Molar Ratio ( $\text{FeCl}_3/\text{Pyrrrole}$ ) (b) temperatures ranging from 303-343K

**Models for Temperature Dependent Conductivity:**

In order to determine the current conduction mechanism in PPy-PVA composite films, the electrical conductivity of all four films have been determined in the temperature range from 303K to 343K. The electrical conductivity of all four samples increases with the increase in temperature exhibiting the semiconducting nature of these samples. This behaviour of electrical conductivity can be explained using two different models:

**I. Arrhenius (thermally activated) Model:**

Plots of  $\ln(\sigma)$  as functions of  $1000/T$  is shown in Figure 4. This type of electrical conductivity behavior follows Arrhenius model [22] and according to this model conductivity temperature relation is

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \tag{2}$$

Where:  $\sigma$  is conductivity,  $\sigma_0$  is constant,  $E_a$  is activation energy,  $k$  is Boltzmann constant ( $8.617\ 3324 \times 10^{-5}$  eV  $\text{K}^{-1}$ ),  $T$  is Temperature.

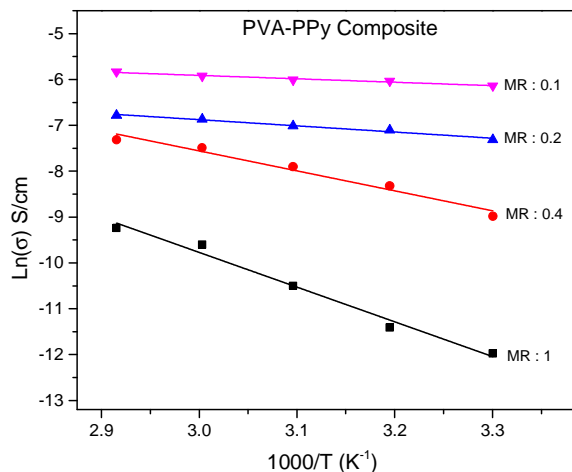


Figure 4. Plots of  $\ln(\sigma)$  as functions of  $1000/T$

Figure 4 shows that the conductivity value when plotted as  $\ln(\sigma)$  versus  $1000/T$  exhibits linear dependency. Solid lines show linear fit of experimental data obtained at different temperatures. Linear regression value which indicate the best fit are given in Table 2, from which we can conclude that the conductivity exhibits a thermally activated

process overtemperature range of 303K -343K.Activation energy ( $E_a$ ) is calculated from slope of these plots. The obtained activation energies are also given in Table 2 which are found to be in agreement with the literature [23].

**II. Mott variable-range hopping (VRH) Model:**

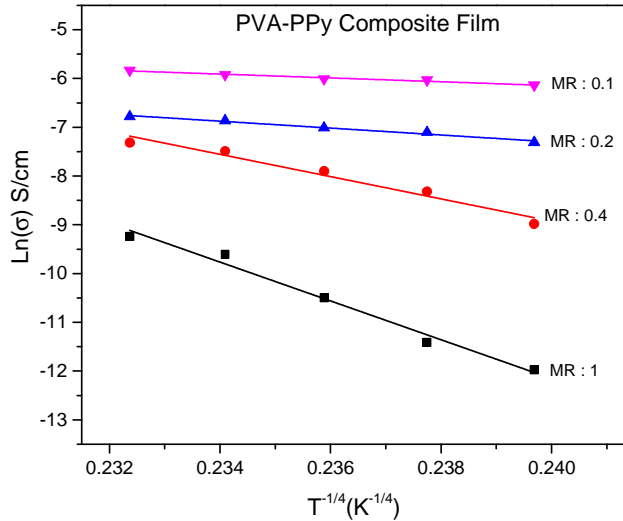


Figure 5.Plots of Ln ( $\sigma$ ) as functions of  $T^{-1/4}$ .

Mott variable-range hopping, is a model describing low-temperature conduction in strongly disordered systems with localized charge-carrier states.Since disorder plays an important role in conducting polymers, Variable Range Hopping (VRH) is also considered as one of the major carrier transport mechanism. According to this model thecharacteristic temperature dependence of conductivity isgiven by [24]

$$\sigma = \sigma_0 \exp \left[ - \left( \frac{T_0}{T} \right)^{1/(1+d)} \right] \tag{3}$$

Where  $\sigma$  is conductivity,  $\sigma_0$  constant,  $k_B$  is Boltzmann constant, T is Temperature,  $d = 1, 2, 3$  is the dimensionality of the conducting process and  $T_0$  is associated with the degree of localization of the electronic wave function

In order to evaluate the possibility of Mott’s VRH and dimensionalityof conduction process in polymeric films, logarithmic plot of dc conductivity as a function of  $T^{-1/4}$  should follow a straight line.The plots of Ln ( $\sigma$ ) as functions of  $T^{-1/4}$  are shown in Figure 5, which shows that  $d= 3$  give straight lines. This type of electricalconductivity behavior follows Mott variable-range hopping (VRH) Model.This point indicates that the transport mechanism in PPy conducting polymer correspondsto 3-dimensional process. The values of the linear regression are calculated for different mechanisms as given in Table 2.

Table 2. Values of linear regression with different mechanisms and activation energy

Transport mechanism	Linear Regression			
	MR : 0.1	MR : 0.2	MR : 0.4	MR : 1
Thermal Activation and Activation Energy (eV)	0.98046	0.96384	0.9774	0.95956
Mott’s 3D VRH	0.65231	0.37533	0.11624	0.064381

For three dimensional transport hopping parameters to be given by[25] are

$$T_0 = \left[ \frac{18}{r_0^3 k N(E_F)} \right] \tag{4}$$

where  $r_0$  is localization length,  $k$  is Boltzmann constant,  $N(E_F)$  is density of states at Fermi level.

Hopping distance (R) and average hopping energy (W) were defined by Mott and Davis as

$$R = \left[ \frac{9r_0}{8\pi N(E_F)kT} \right]^{1/4} \quad (5)$$

and

$$W = \left[ \frac{3}{4\pi R^3 N(E_F)} \right] \quad (6)$$

The hopping parameters were determined from the experimental data plotted in Figure 5 using equations (4-6) and are given in Table 3.

**Table 3. The values of Variable Range Hopping (VRH) parameters**

Sample	VRH parameters			
	$T_0$ (K)	$N(E_F)$ (eV/cm)	R (cm)	W (eV)
MR : 0.1	$2.5141 \times 10^{10}$	$8.31 \times 10^{15}$	$3.6477 \times 10^{06}$	0.59199
MR : 0.2	$2.7320 \times 10^9$	$7.65 \times 10^{16}$	$2.0943 \times 10^{06}$	0.33989
MR : 0.4	$2.5233 \times 10^7$	$8.28 \times 10^{18}$	$6.4926 \times 10^{07}$	0.10537
MR : 1	$2.3956 \times 10^6$	$8.72 \times 10^{19}$	$3.6039 \times 10^{07}$	0.05849

## CONCLUSION

The synthesis of flexible and free standing PVA-PPy-FeCl<sub>3</sub> composite films was achieved. The composite showed good film forming ability on flat glass petri dish or polypropylene surface and has best storage ability. The dc electrical conductivity ( $\sigma$ ) of the composite polymer films have been investigated in the temperature range from 303K to 343K and it was observed that  $\sigma$  varied from  $0.63108 \times 10^{-5}$  S/cm to  $2.16 \times 10^{-3}$  S/cm at room temperature, as the Molar Ratio varied from 0.1 to 1.00. The electrical conductivity increased with increase in dopant concentration and temperature. Activation energies of the charge carriers were obtained ranging from 0.65231eV to 0.064381eV. The density of states at Fermi level, average hopping distance and hopping energy have been calculated. It is found that composite film conduction mechanism follows the Arrhenius model as well as Mott's 3D variable range hopping (VRH) model in the studied temperature range.

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