

# Effect of Oxidizing Agent on the Ionic Conductivity of Polypyridine- Poly (Vinyl Acetate) Composite Films

A. V. Kohale

Department of Physics, Shri R. R. Lahoti Science College, Morshi, India

## ABSTRACT

An attempt has been made to investigate the effect of temperature and concentration of ferric chloride ( $\text{FeCl}_3$ ) oxidant on the conductivity of polypyridine (PPY)-poly (vinyl acetate) (PVAc) composite films and to study the structure of these films. Polypyridine (PPY) and poly vinyl acetate (PVAc) composite films were synthesized by chemical oxidative polymerization method with the solution of ferric chloride ( $\text{FeCl}_3$ ) oxidant in methanol at room temperature. Their dc conductivity as a function of temperature (308-353 K) was measured. At the room temperature (308 K), the dc electrical conductivity of the films initially increases with concentration of  $\text{FeCl}_3$  and becomes maximum ( $\sigma = 1.57 \times 10^{-11} \text{ S/cm}$ ) at 25 wt % of  $\text{FeCl}_3$ , which indicates percolation behaviour. This increase in conductivity is due to increase in strength of oxidizing agent, which increases the rate of polymerization. However, further increase in concentration of  $\text{FeCl}_3$ , decreases the conductivity of the films due to reduced segmental motion of polymer. V-I characteristics of the films were linear, indicates the ohmic nature. The temperature dependence of conductivity shows Arrhenius behaviour. The composite films have been characterized by X-ray diffraction. The XRD spectra of the films reveal a broad hump in low  $2\theta$  region typical of short range order indicating that these films are amorphous.

**Keywords :** PPY-PVAc composite, Chemical oxidative polymerization, XRD, dc conductivity

## I. INTRODUCTION

Polymers, which have special properties, is a field of increasing scientific and technical interest and offer a challenging opportunity to polymer scientist to develop the broad variety of new materials for specific use. The characteristic properties of the organic high performance polymers are electrical and magnetic properties though the polymers are technically insulators. However the question of producing polymers that exhibits electrical conductivity similar to metals has always drawn attention of the polymer scientists. Since such polymers combine the electrical properties of metals with the advantages such as light weight, easy processibility, resistance to corrosion and chemicals at low cost.

Conducting polymers is a relatively new class of materials. During last two decades, researchers succeeded in synthesizing polymers, which have high electrical conductivity. At present many such polymers including polypyrrole (PPy), polyphenylene sulphide (PPS), polyethylene sulphide (PES), polythiophene (PTh), polyaniline (PAn), polypyridine (PPY), etc. have been discovered. Recently multicomponent conducting polymer blends and composites have been prepared which have wide range of conductivity.

Many research workers have studied synthesis and charge transport in composites and blends like

Polypyrrole-polyvinyl chloride (PPy-PVC) [1], PPy-Ferric oxide nanocomposites [2], PPy- polyvinyl acid (PPY-PVA) [3], polystyrene-polyaniline (PS-PAn) [4] and PPy- poly (alkyl methacrylates) [5]. Most of them explained the charge transport behavior as a charge carrier hopping (Mott's VRH) between localized states while in case of ionically conducting solid polymer electrolytes, the conductivity is found to be temperature dependent and is more completely explained by the VTF (Vogel-Tamman-Fulcher) equation [6-8].

Still, polypyridine is less studied polymer as compared to others and hence an attempt is made to study conduction mechanism in PPY-PVAc composite films. These films were synthesized by oxidative chemical polymerization. Hence effect of strength of oxidizing agent and temperature on electrical conductivity of PPY-PVAc composite films was studied.

## II. EXPERIMENTAL

PPY was synthesized at room temperature (308 K). A mixed solution of PVAc (AR grade) and FeCl<sub>3</sub> (E. Merck) was first prepared in methanol (AR grade). PVAc and methanol were taken in 10: 90 ratio to obtain thin films. Then pyridine monomer was added to the solution, in such a way that pyridine to PVAc ratio was constant. To study the effect of oxidizing agent, concentration of FeCl<sub>3</sub> was changed from 10 wt% to 80 wt% with respect to pyridine. It gives the dark brownish homogeneous solution which was then poured on chemically cleaned and plane glass substrate to prepare the films of composite. Polymerization of pyridine, which was suppressed in a mixed solution, progressed rapidly due to an increase of oxidation potential caused by evaporation of solvent. Initially this solution was homogeneous but phase separation takes place as the polymerization of pyridine proceeds. PPy aggregates were connected with each other, which resulted in PPy networks

throughout the composite. After sufficient drying, films were washed with water to remove the excess FeCl<sub>3</sub>. Thickness of these films was measured with digital micrometer (Digimatic, Japan having L.C.  $\pm 1\mu\text{m}$ ) and it is in the range of 50 to 250  $\mu\text{m}$ .

The X-ray diffractograms were obtained using X-ray diffractometer PANalytical PW: 3040/60, Netherland. The Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) was used. Samples were scanned over a wide range of Bragg's angles  $5 \leq 2\theta \leq 90^\circ$ .

For dc electrical conductivity measurement circular films with radius ( $\approx 1.5 \text{ cm}$ ) and thickness ranging from 100 to 200  $\mu\text{m}$  was used. The composite film was sandwiched between two copper electrodes and then placed in a muffle furnace. A dc regulated power supply and a Pico ammeter having resolution of 1 pA was used for measurement. DC electrical conductivity was measured in the temperature range 308- 358 K. The heating rate of the sample was maintained at 2°C/min. The electrical conductivity is subsequently obtained from the relation

$$\sigma = t / R_b.A$$

Where, t is the thickness of the film, A is the cross sectional area of the electrodes and R<sub>b</sub> is the bulk resistance of the film.

## III. RESULTS

### 3.1 X-Ray diffraction

The X-ray diffraction patterns of PPY-PVAc composite films with different wt % of FeCl<sub>3</sub> are shown in figure 1. Diffraction patterns obtained in the 2 $\theta$  range between 10 and 90 degrees, which are similar and without any sharp diffraction peaks. The absence of peak represents complete amorphous nature of the sample. All spectra for different FeCl<sub>3</sub> wt% reveal a broad hump in the low 2 $\theta$  region. It is due to short range order and indicating that these PPY-PVAc

films are amorphous. Increase in concentration of oxidizing agent FeCl<sub>3</sub> does not induce any crystallinity in these composite films.

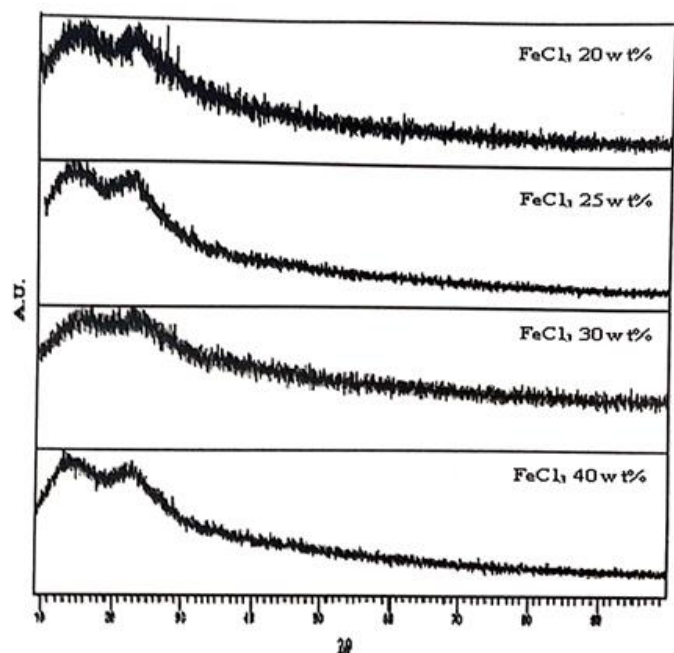


Fig. 1 XRD spectra of PPY-PVAc composite films with different FeCl<sub>3</sub> wt %

### 3.2 DC Conductivity

The variation of dc conductivity with concentration of FeCl<sub>3</sub> wt % for PPY-PVAc composite films at T=323 K is shown in figure 2.

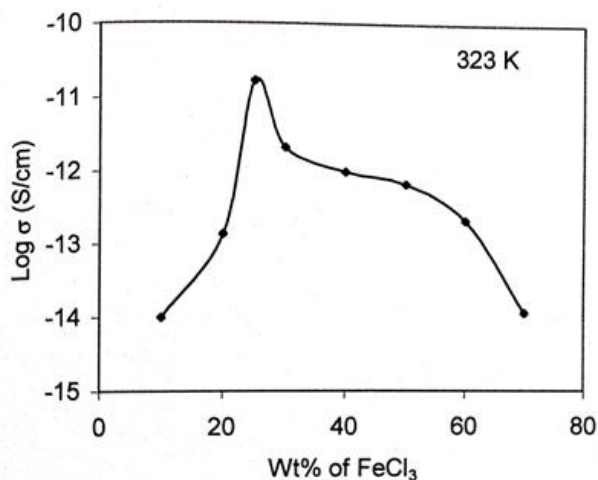


Fig. 2 Variation of dc conductivity with FeCl<sub>3</sub> wt %

Initially the conductivity increases, reaches to  $1.57 \times 10^{-11}$  S/cm for 25 wt % of FeCl<sub>3</sub> and then decreases with further increase in FeCl<sub>3</sub> concentration. Many researchers [9-11] reported a similar bell shaped conductivity isotherm with respect to oxidant concentration. In case of polypyrrole composite [5, 10-13] percolation behavior was obtained even for low concentration of polypyrrole. Increase in conductivity with FeCl<sub>3</sub> was explained on the basis of formation of polypyrrole conducting network due to well dispersed polypyrrole in the structure of composite.

Figure 3 shows the Arrhenius plot of PPY-PVAc composite films. This gives the temperature dependence of dc conductivity of composite films and follows the equation:

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

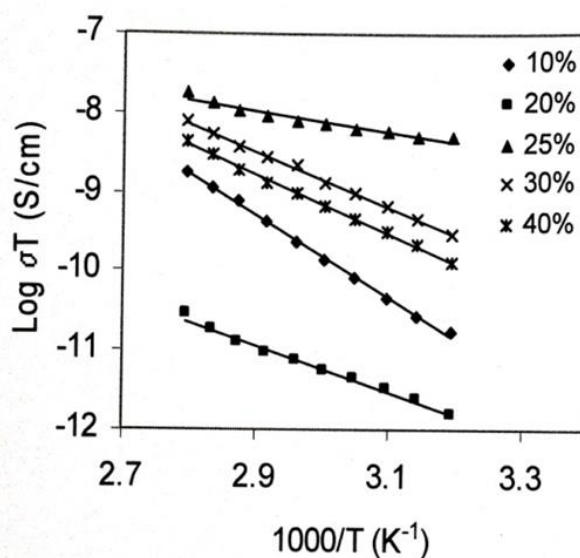


Fig.3 : Arrhenius plots of PPY-PVAc composite films

From this plot it is observed that the conductivity increases with increase in temperature. As the temperature increases, mobility of the ions increases, which results the rise in conductivity. The conductivity is found to be maximum for 25 wt % of

FeCl<sub>3</sub>. All the plots are linear; hence it follows Arrhenius law. The slope of the Arrhenius plot decreases suggesting that activation energy for conduction decreases. The activation energies for conduction and pre-exponential factor for different FeCl<sub>3</sub> wt % are given in following table 1.

**Table 1 :** Arrhenius fitting parameters for different FeCl<sub>3</sub> wt %

S. N.	FeCl <sub>3</sub> (wt %)	Activation energy E <sub>a</sub> (eV)	Pre-exponential factor σ <sub>0</sub> (S/cm)
1	10	0.44	6.02 X 10 <sup>5</sup>
2	20	0.25	3.57 X 10 <sup>-3</sup>
3	25	0.13	6.86 X 10 <sup>-5</sup>
4	30	0.29	3.22 X 10 <sup>1</sup>
5	40	0.32	9.57 X 10 <sup>1</sup>

The variation of activation energy with concentration of FeCl<sub>3</sub> is shown in figure 4.

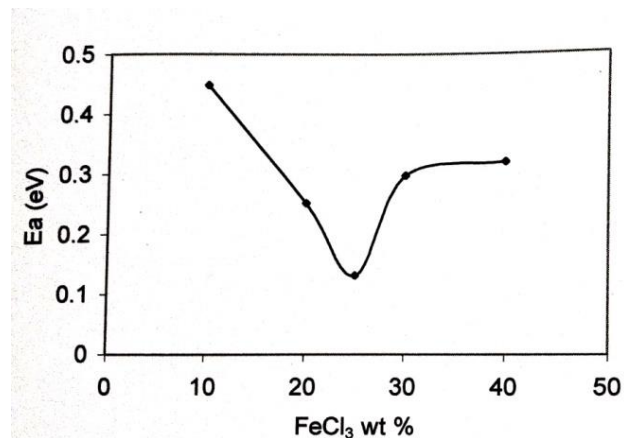


Fig. 4: Variation of activation energy with FeCl<sub>3</sub> wt %

It is observed that value of activation energy decreases with FeCl<sub>3</sub> wt % and again increases for higher concentration of FeCl<sub>3</sub>. The activation energy is minimum for 25 wt % of FeCl<sub>3</sub> indicates that the charge carriers require minimum energy to hop along conducting network and shows maximum conductivity. Composite films with lower concentration than 25 wt % and also of higher

concentration offer high resistance to hopping of charge carriers and shows higher value of activation energies.

In PPY-PVAc composite FeCl<sub>2</sub><sup>+</sup> ions may get coordinated with nitrogen of the PPY. This type of interaction with FeCl<sub>2</sub><sup>+</sup> may be considered because positively charged nitrogen will be electronically stabilized by delocalization through the conjugated electrons of PPY chains. Such interaction may result in the formation of FeCl<sub>4</sub><sup>-</sup> ions.

The increase in FeCl<sub>3</sub> concentration increases the loading of PPY in the composite, which ultimately leads to coordination of more FeCl<sub>2</sub><sup>+</sup> ions with nitrogen of PPY chains. Therefore overall effect of FeCl<sub>3</sub> is to increase the FeCl<sub>4</sub><sup>-</sup> ions in the composites. The maximum conductivity of PPY-PVAc composite, for 25 wt % of FeCl<sub>3</sub> may be attributed to the well dispersed positively charged PPY chains in the PVAc phase. Because well dispersed network of PPY chains in the PVAc phase leads to enhance the mobility of FeCl<sub>4</sub><sup>-</sup> ions. On other hand PVAc-FeCl<sub>3</sub> complex may become more and more rigid at high concentration of FeCl<sub>3</sub>, which ultimately reduces the segmental motion of polymer. The reduced segmental motion, reduces the mobility of FeCl<sub>4</sub><sup>-</sup> ions and hence the conductivity decreases with further increase in concentration of FeCl<sub>3</sub>. Thus the overall effect of increase in concentration of FeCl<sub>3</sub> from 10 wt % to 25 wt % is to increase the loading of PPY in the composite which ultimately enhance the mobility of the FeCl<sub>4</sub><sup>-</sup> ions and hence the conductivity. But further increase in FeCl<sub>3</sub> concentration (for 30 and 40 wt %) shows the increase in conductivity.

#### IV. CONCLUSION

PPY-PVAc composite were synthesized by chemical oxidative polymerization of pyridine by different wt % of oxidizing agent FeCl<sub>3</sub>. Conductivity measurement reveals that the conductivity depends on FeCl<sub>3</sub> wt %.

It is observed that the conductivity is maximum at 323 K for PPY-PVAc composite, synthesized with 25 wt % FeCl<sub>3</sub>. PPY in the PPY-PVAc composite is anticipated to enhance the ionic transport. The initial increase in conductivity with FeCl<sub>3</sub> wt % may be due to FeCl<sub>4</sub><sup>-</sup> ions, as they become more mobile due to coordination of FeCl<sub>2</sub><sup>+</sup> from the ions with nitrogen from the PPY. Further increase in FeCl<sub>3</sub> wt %, decreases the conductivity. This may be due to segmental motion of PVAc. Conductivity is found to be temperature dependent. The temperature dependence of conductivity of PPY-PVAc composite follows Arrhenius law. The activation energy for conduction is found to be minimum for 25 wt % FeCl<sub>3</sub> indicates that charge carriers require minimum energy to hop along conducting network and shows maximum conductivity. The X-ray diffraction patterns of PPY-PVAc composite films are without sharp peaks indicating amorphous nature of the samples.

## V. ACKNOWLEDGEMENT

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