Study of Conduction Mechanism in Polypyridine - Poly(Vinyl Acetate) Films By Transference Number

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ABSTRACT

The effect of concentration of ferric chloride ($FeCl_3$) oxidant on transference number of polypyridine-polyvinyl acetate films has been described. Polypyridine (PPY) and poly vinyl acetate (PVAc) composite films were synthesized by chemical oxidative polymerization method with the solution of ferric chloride ($FeCl_3$) oxidant in methanol. The transference number for PPY-PVAc films synthesized with different concentration of $FeCl_3$ was determined by Wagner's dc polarization technique. The transference number for the films prepared with 10, 20, 25, 30 and 40 wt% of $FeCl_3$ lies between 0.51 to 0.80. It is found that, the transference number increases with the increase in concentration of $FeCl_3$. This increase is due to increase of ion concentration in PPY-PVAc composite.

Keywords : PPY-PVAc composite, Chemical oxidative polymerization, Transference number.

I. INTRODUCTION

In last few decades, there has been a great deal of increasing interest in the synthesis and characterization of conducting polymers because of their applications in organic batteries, sensors, microelectronic devices, electrocatalysis and also their electrical, electrochemical and optical properties[1].

Earlier the blends of PVC and PPy were prepared by oxidative chemical polymerization of pyrrole with an oxidizing agent $FeCl_3$. Ionic conductivity study of such material was carried out and studied the effect of oxidizing agent on conductivity of the films [2]. Polypyridine is a recent addition to the list of conducting polymers. It is of particular interest because it is soluble, thus, processable material even in its unsubstituted state, yet being chemically stable. It is considered as an important candidate material for application in light- emitting polymeric diodes.

Many research workers have studied synthesis and charge transport in composites and blends like PPy-polyvynil chloride (PPy-PVC) [3], PPy-Ferric oxide nanocomposites [4], PPy- polyvynil acid (PPY-PVA) [5], polystyrene-polyaniline (PS-PAn) [6] and PPy-poly (alkyl methacrylats) [7]. 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) equatiton [8-10].

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.

II. METHODS AND MATERIAL

PPY was synthesized at room temperature. A mixed solution of PVAc (AR grade) and FeCl₃ (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 FeCl₃ 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 s 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 FeCl₃. Thickness of these films was measured with digital micrometer (Digimatic, Japan having L.C. ± 1µm) and it is in the range of 50 to 250 µm.

The ionic/electronic transference number can be defined as:

$t_{ion} = \sigma_{ion} / \sigma_T = I_{ion} / I_T$ …………..(1)

$t_{ele} = \sigma_{ele} / \sigma_T = I_{ele} / I_T$ …………..(2)

Where, $\sigma_{ion} / \sigma_{ele}$ and I_{ion} / I_{ele} are the conductivity and current contribution due to ions / electrons respectively. Transference number gives quantitative information about the contribution of electronic and ionic conduction to the total conductivity.

Wagner's dc polarization technique [11] was used to measure the ionic/electronic transference number. In this technique, PPY-PVAc film was sandwiched between nonblocking (silver) and blocking (graphite) electrodes. A constant dc voltage 1 V was applied across the sample with help of dc regulated power supply and corresponding current (pA) was measured as a function of time at room temperature.

III. RESULTS AND DISCUSSION

The current versus time plots of the PPY-PVAc composite films are obtained which exhibit typical behavior of ionic charge transport. Current versus time plots for some of the samples prepared with 10, 20, 25, 30 and 40 wt% of FeCl₃ are shown in figure 2 (a), (b), (c), (d) and (e) respectively.
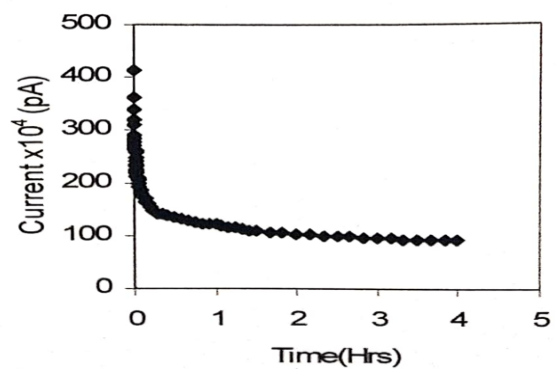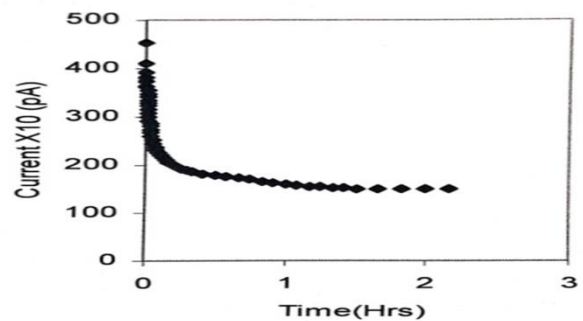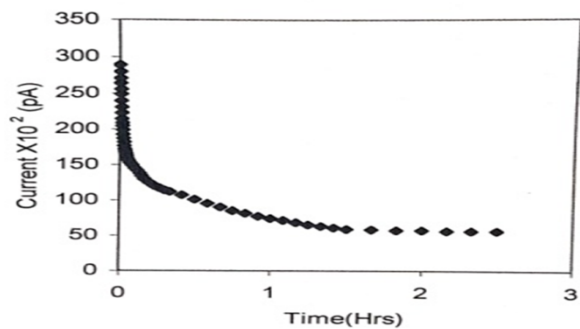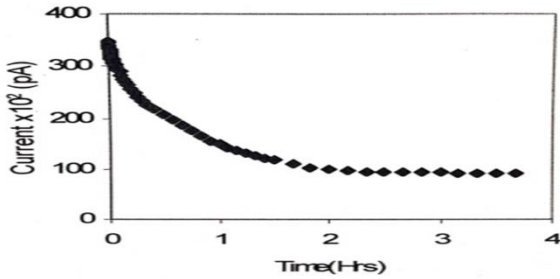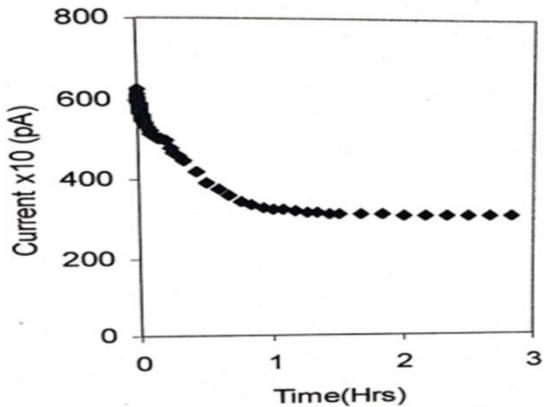

Fig. 2 (a)

Fig. 2 (b)

Fig. 2 (c)

Fig. 2 (d)

Fig. 2 (e)

Fig. 2 Polarization current as a function of time for different FeCl3 wt % films

From figure 2, it is observed that, the total current becomes nearly almost constant at some non-zero value after some time. The final residual current is mainly due to electrons/holes. The ionic and electronic transference numbers were calculated separately from the polarization current versus time plots using equations (1) and (2). Transference numbers for different FeCl₃ concentrations are given in the following table 1.

Table 1: Ionic transference number for different FeCl₃ wt %

Sr. No.	FeCl₃ wt %	Ionic transference number (t_{ion})
1	10	0.51
2	20	0.67
3	25	0.77
4	30	0.73
5	40	0.80

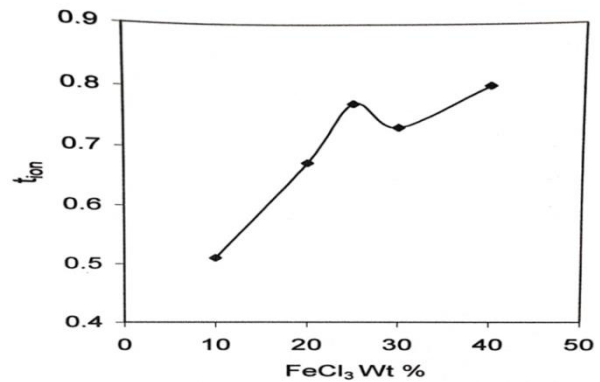The variation of transference number with concentration of FeCl₃ is shown in figure 3.

Fig. 3 Variation of transference number with FeCl3 wt %

The values of transference number increase with the increase in concentration of FeCl3. For 10 wt % FeCl3 transference number is 0.51, while for 40 wt % it becomes 0.80. This suggests that the charge transport in the PPY-PVAc composite, synthesized with higher concentration of FeCl3 is predominantly due to ions. While for the films with low concentration of FeCl3 shows both ionic and electronic charge transport. Initially ionic transference number (tion) increases with FeCl3 concentration due to increase of ion concentration in PPY-PVAc composite. For further increase in FeCl3 concentration ionic transference number decreases. This may be due to decrease in ionic mobility, which depends on segmental motion of polymer chain. Due to higher concentration of FeCl3, PVAc – FeCl3 complex become more rigid which ultimately reduces the segmental motion.

IV.CONCLUSION

PPY-PVAc composites were synthesized by chemical oxidative polymerization of pyridine by different wt % of oxidizing agent FeCl₃. The transference number study results that the charge transport in PPY-PVAc composite is predominantly due to ions for higher

$FeCl_3$ wt %. For further increase in $FeCl_3$ concentration ionic transference number decreases. This may be due to decrease in ionic mobility, which depends on segmental motion of polymer chain.

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