

Preparation and Characterization of Fe⁺⁺⁺ -Doped Dipyrindine Polyvinyl Acetate Supported Composite Films

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Abstract

Polypyridine and their composites are attractive materials for the use in existing and emerging technologies because of their light weight, low cost and photoluminescence properties. In the present paper, we focused on the structural properties of Fe⁺⁺⁺ -doped Dipyrindine Polyvinyl acetate supported composite films where in PVAc as the host matrix. Dipyrindine-PVAc composite thin films were synthesized by chemical oxidative polymerization method with the solvent methanol and ferric chloride (FeCl₃) as an oxidant as well as dopant. All films were characterized using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) spectroscopy. The thermal properties are studied through TG and DTA technique. Broad peaks are observed in the range of $2\theta = 12$ to 30° in X-ray spectra, which are due to scattering of X-rays from the dipyrindine chain at the interplaner spacing. Almost 99 % amorphous nature of all samples is seen from the Scanning Electron micrographs which also reflected in the XRD spectra. In FTIR spectra the absorption peaks at 1456 and 1595 cm⁻¹ may associate to typical dipyrindine ring vibration. The broad bands at 1741, 1734 and 1743 cm⁻¹ for samples of 20, 25 and 30 wt % FeCl₃ respectively occurred which confirm the presence of PVAc in the samples.

KEYWORDS: Composites, Dipyrindine, X-RD, SEM, FTIR

1. Introduction:

Conductive polymers and their composites represent a potential for semiconductor technology. The mechanism of charge transfer between organic, inorganic, semiconductors and conductive polymers has been recently investigated by Halliday [1]. Unusual properties of these polymers have led to extensive research resulting in better understanding and numerous commercial applications. Conductive polymers can be synthesized by filling an insulation polymer matrix with conducting particles such as metal flakes or metalized fibers, by chemical or electrochemical method to produced intrinsically conductive polymers.

Many polymer composites can be doped with either electron acceptors or electron donors to increase their electrical conductivity. Pyridine based polymers have attracted much interest because of their oxidative stability and electron transport properties which make them promising candidates for polymer-based LED applications. Polymer composites of conductive polymers such as polyacetylene, polypyrrole, polythiophene and polyaniline have also been reported in the literature [2-4].

This paper focuses on the synthesis of Dipyrindine-PVAc composite films prepared by chemical oxidative polymerization method using FeCl₃ as oxidizing agent as well as doping material. All films were characterized using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) spectroscopy.

2. Experimental

2.1 Materials

Chemically polymerized Dipyrindine-PVAc supported composite films were obtained at room temperature by oxidative polymerization using AR grade FeCl_3 as oxidant and monomer pyridine (E. Merck, Germany) and polyvinyl acetate (PVAc) AR grade (Poly Chem. Industries, Mumbai).

2.2 Preparation of samples

For the preparation of Dipyrindine-PVAc composite films using FeCl_3 as oxidizing agent as well as dopant, a mixed solution of PVAc and methanol (10:90) was prepared. In order to make the homogenous solution 1 mole FeCl_3 was added (during this process heat is evolved therefore the process is said to be exothermic) and stirred about 30 minutes. Finally the monomer pyridine was added. The maximum yield was obtained by varying the concentration of pyridine monomer. Then in order to know the effect of oxidizing strength of FeCl_3 , to form conducting path, the concentration of FeCl_3 was change from 10 to 50 wt %. When monomer pyridine was added to the solution of PVAc, methanol and FeCl_3 , a yellow white homogeneous solution was obtained. Now the homogeneous solution was poured on the chemically cleaned optically plane glass plate to prepared films of the composites. The whole assembly was placed in a dust free chamber maintained at constant temperature. In this manner Dipyrindine-PVAc composite films were prepared by isothermal evaporation technique [5].

2.3 X-Ray diffraction (X-RD)

The prepared polymer composite films were characterized by X-RD (Philips XPERT-PRO). The X-ray diffraction spectra of samples was recorded on X-ray diffractometer using $\text{CuK}\alpha$ ($\lambda = 1.5406\text{\AA}$). The diffractogram was recorded in terms of 2θ in the range of 3 to 100° at room temperature.

2.4 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is a convenient technique to study the microstructure of the thin films. Surface morphological study of optimized Dipyrindine-PVAc supported composite films was done by using scanning electron microscope (JEOL-JSM- 6380A, analytical scanning electron microscope) operating with an accelerating voltage of 15 KV at Vishweshwarreya National Institute of Technology, Nagpur. All samples were coated with gold prior to measurement by using sputtering unit (JEOL-JFC- 1600 auto fine coater). Grain size of the films was determined from SEM photograph at different magnifications.

2.5 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is the most widely used method for characterizing the molecular structure of polymers. The FTIR spectrum of all Dipyrindine-PVAc composite films was recorded on Perkin Elmer FTIR Spectrophotometer at room temperature in the wavelength range 4000 to 450 cm^{-1} using KBr pellet. All spectra were carried out at Department of Materials Engineering, Vishweshwarreya National Institute of Technology, Nagpur.

3. Results and discussion

3.1 XRD spectra

The X-ray diffraction patterns of prepared Dipyrindine-PVAc supported composite films are shown in figure 1. X-ray diffraction pattern shows 99 % amorphous nature of the samples. The broad peaks are observed in the 2θ range of 12 to 30° . Which are due to scattering of X-rays from the Dipyrindine chain at the interplaner spacing [6]. The small reflections at $2\theta = 31, 37, 46, 59$ and 66° indicate the presences of ferrous in Dipyrindine-PVAc composite films [7].

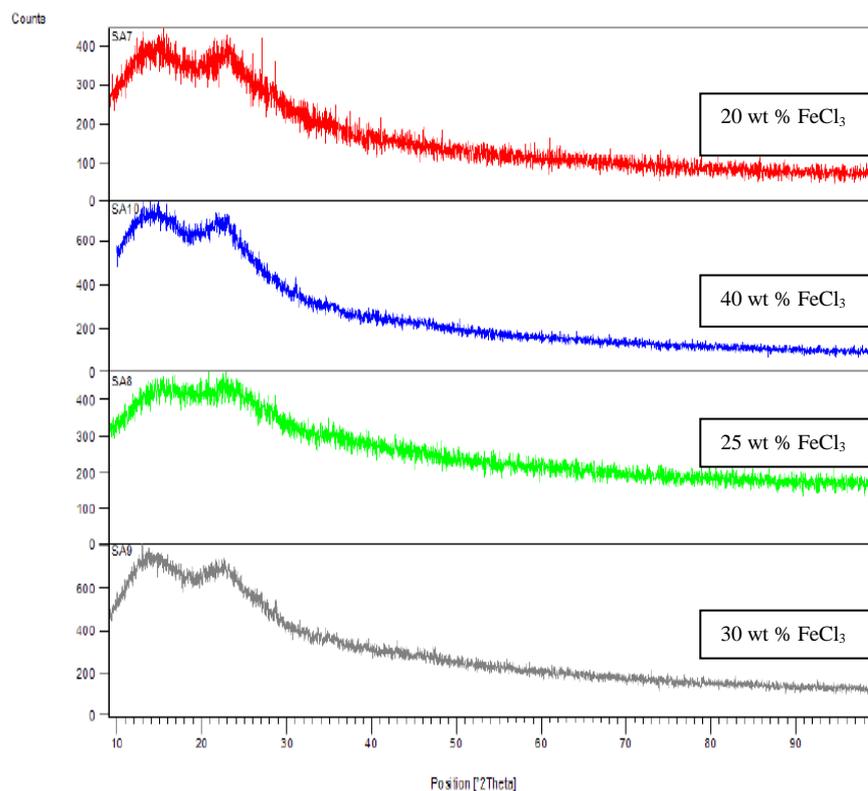


Figure 1: XRD spectra of Dipyridine-PVAc supported composite films

3.2 Scanning Electron Microscopy (SEM)

The surface morphology of Dipyridine-PVAc composite films with different concentration of oxidizing agent was analyzed by SEM and the pictures are shown in figures 2 (a), (b) and (c) for 20, 25 and 30 wt % FeCl_3 respectively. Almost 99 % amorphous nature of all samples (20, 25 and 30 wt % FeCl_3) is seen from the micrographs. This nature is also reflected in the XRD spectra. Approximate 1 % crystallinity is seen from micropictures as in XRD. The phases so obtained are due to FeCl_3 that remain as dopant in Dipyridine-PVAc composite films. The figure 2 (a and b) shows uniform crystals of FeCl_3 of size varies from ~ 1.5 to $3 \mu\text{m}$. The non uniform porous and voids are seen. The porous size varies from ~ 1 to $1.5 \mu\text{m}$. The more crystallite nature is seen in figure 2 (c) where FeCl_3 content is more. The crystalline size seen from micrographs varies from ~ 0.9 to $1 \mu\text{m}$.

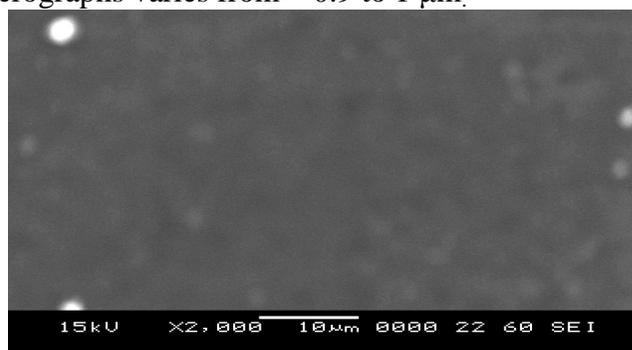


Figure 2(a) 20 wt %

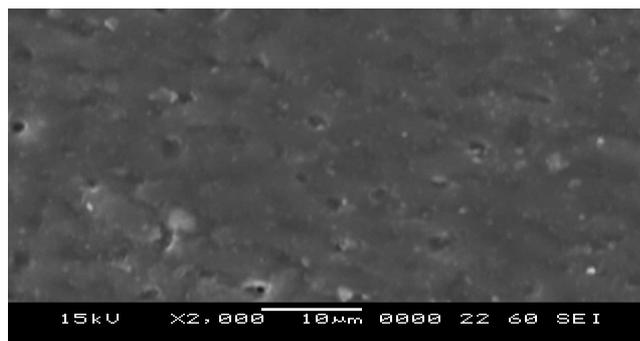


Figure 2(b) 25 wt %

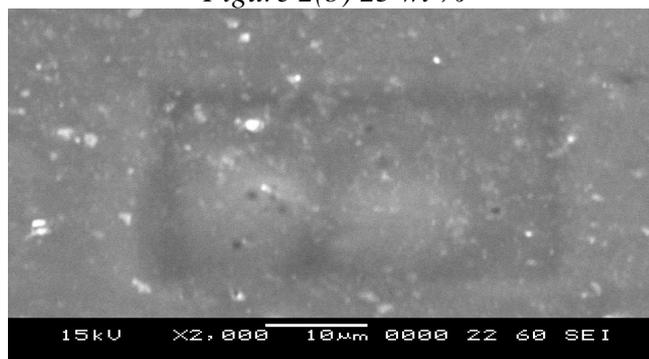


Figure 2(c) 30wt %

Figure 2: SEM photographs of Dipyridine-PVAc supported composite films of a) 20, b) 25 and c) 30 wt % FeCl₃.

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy is the most widely used method for characterizing the molecular structure of polymers. By using IR spectroscopy it is possible to distinguish the different repeat unit structure that can arise from polymerization.

Infrared spectra of Dipyridine-PVAc supported composite films is given in figure 3. The corresponding absorption peak frequencies of all samples are tabulated in table 1. The spectral studies of all prepared composite films show the number of absorption peaks. The peaks are sharp, medium and broad. From FTIR spectra of all investigated films it is observed that the basic structure of the polymer composite is same though the oxidizing strength of FeCl₃ is different.

The infrared spectra of all Dipyridine-PVAc supported composite films (FeCl₃ as oxidizing agent as well dopant) show the eleven absorption bands and these values are listed in table 1. Under the experimental conditions the polymerization of pyridine is restricted only dimerization occurred, in which the two pyridine rings directly get bonded via nitrogen as there is no other substituent in the pyridine ring. This dimer involved O-H group of PVAc as observed from complete absence of O-H stretched in FTIR spectra. Moreover nitrogen oxygen N-O stretched can be suggested around 1456 to 1595 cm⁻¹ [8]. This suggested that PVAc provides a base for attachment of dimerized pyridine. The absorption bands at 830 to 500 cm⁻¹ are assigned to the presence of metal oxide (Fe atoms) in the composite material and may correspond to C-Cl vibrations [9]. Incorporation of Fe atoms in the dimerized pyridine-PVAc composites is possible only when the nitrogen atoms of dimerized pyridine are involved in the co-ordination of Fe atoms. Absorptions at 1110 to 1118 and 1015 to 1017 cm⁻¹ are assigned to C-N stretching [10] and absorption peaks at 1370 to 1389 cm⁻¹ corresponds to C-C stretching, which are induced by the trace amount of PVAc

present in the composite films [11]. The spectrum is similar to the standard IR spectrum of PVAc (Card No. 187-189) [12]. Two absorption peaks at 1456 and 1595 cm^{-1} may associate to typical Dipyrindine ring vibration. The broad band at 1741, 1734 and 1743 cm^{-1} for samples 20, 25 and 30 wt % FeCl_3 respectively occurred which confirm the presence of PVAc in the samples [13]. Dipyrindine-PVAc supported composite film shows two stretching bands, asymmetric and symmetric at 2854 and 2855 cm^{-1} and 2924 and 2925 cm^{-1} associating with C-H stretching [14]. A small peaks obtained at 3280 and 3317 cm^{-1} in samples 20 and 25 wt % FeCl_3 which are due to water molecule or OH group [15]. This is obvious because FeCl_3 is hygroscopic and it is used as oxidant as well as dopant in the samples. The strong bands in the range of 1741 to 880 cm^{-1} show the conductive forms of polymers [16]. For all samples it is also observed that as molar concentration of oxidizing agent (FeCl_3) increases the IR absorption peaks due to stretching vibration shifted toward higher wave number also intensity of the peaks increases.

The probable structure of Fe^{+++} -doped Dipyrindine Polyvinyl acetate supported composites may suggested as shown in figure 4.

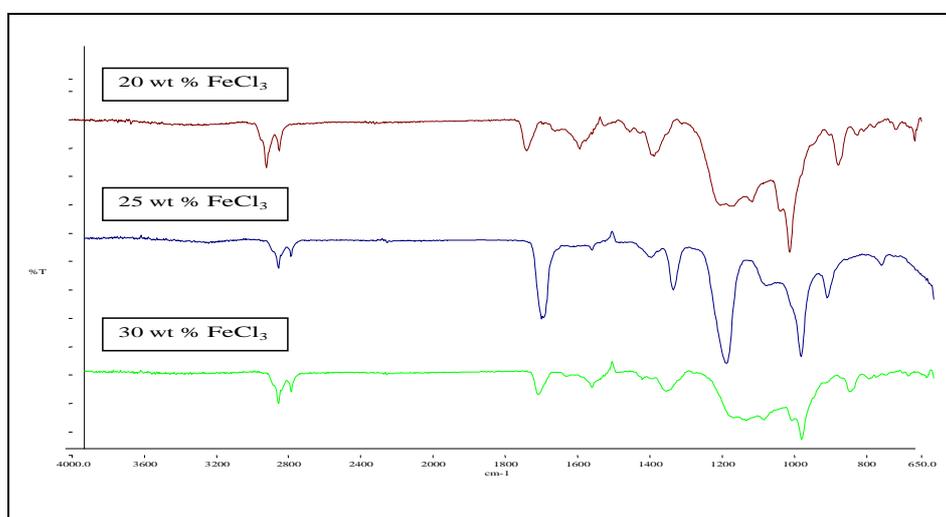


Figure 3: FTIR spectra of Dipyrindine-PVAc composite films of 20, 25 and 30 wt % FeCl_3 .

Table 1: Experimental data from FTIR spectra for Dipyrindine-PVAc composite films

FeCl_3 wt %	Position of absorption maxima. (cm^{-1})										
	810.	827.	1015.0	1118.	1389.	1456.	1595.	1741.	2298.	2854.	292
20	6	3	3	4	2	7	7	9	8	0	4
25	794.	945.	1017.4	1110.	1370.	1457.	1595.	1734.	2323.	2855.	292
	9	3	8	9	2	1	9	8	2	6	5
30	809.	830.	1015.5	1118.	1389.	1456.	1595.	1734.	2325.	2854.	292
	7	2	6	8	2	6	3	0	2	9	4

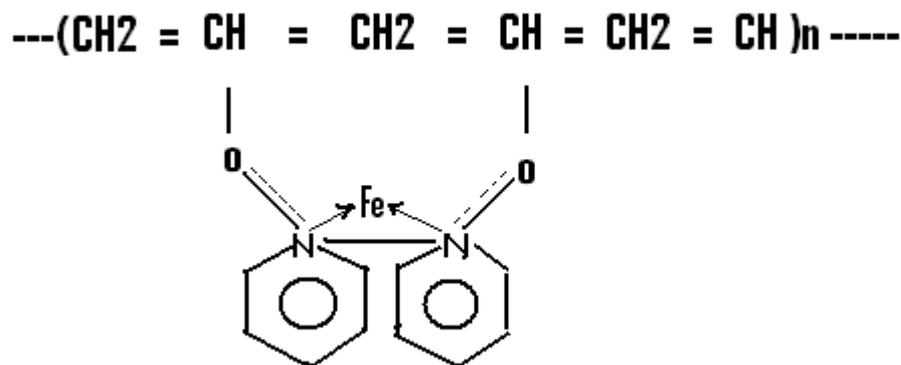


Figure 4: Probable structure of Fe^{+++} -doped Dipyridine Polyvinyl acetate supported composites.

Conclusion:

Characteristics study of Dipyridine-PVAc supported composite films has been made by analyzing the films with XRD, SEM and FTIR. From the XRD spectra of Dipyridine-PVAc composite films, it is observed that all films are amorphous in nature with partial crystalline behavior. The small crystalline peaks are observed only in 30 wt % FeCl_3 sample due to ferrous ions. The surface morphology of Dipyridine-PVAc composite films with different concentration of oxidizing agent was analyzed by SEM. The amorphous nature of all samples is seen in the microphotographs and the partial crystalline behavior is also seen from micropictures as in XRD.

The spectral studies of all prepared composite films were shows the number of absorption peaks. The peaks are sharp, medium and broad. From FTIR spectra of investigated films it is observed that the basic structure of the polymer composite is same though the oxidizing strength is different. The strong bands in the range 1741 to 880 cm^{-1} shows the conductive form of polymer. It is also observed that as molar concentration of oxidizing agent (FeCl_3) increases the IR absorption peaks due stretching vibration increases in intensity and shifted toward higher wave number.

References:

1. D. A. Halliday and E.R. Holland, Thin Solid Films, 276 (1994).
2. Skotheim, Siswoyo, J. ILMU SASAR, 6 (2005) 16-23.
3. C. O. Yoon, M. Reghu, A. Mosen and S. J. Heeger, Phy. Rev. B, 49 (1994) 10851-10863.
4. S. Yigit, L. Toppare and U. Akbulet, Synthetic Met. 79 (1996)
5. R. Bahri and B. R. Sood, Thin Solid Films, 100 (1983) 15
6. E.J. Samuelsen, A.P. Monkman, L.L.A. Pettersson, L.E. Horsburgh and S. Ferrer, Synth. Metals, 124 (2001) 393-398.
7. S. A. Waghule, S. M. Yenorkar and S. P. Yawale, Sensors and Actuators: B Chem- 128 (2008) 366-373.
8. Spectroscopy of Organic Compound, P. S, Kalsi.
9. G. Scrates, IR Characteristics Group of Frequencies, New York (1980)145
10. D. H. William and I. Fleming, Spectroscopic Methods in Organic Chemistry, New Delhi (2004) 57
11. R. Devi, P Purkayastha P. K. Kalita and B. K. Sharma, Bull. Mat. Sci. 30 (2) (2007) 123-128.

- 12 Pushpa Ann Kurian, C. Vijayan, C. S. Suchand, Reji Philip and K. Sathiyamoorthy, *Nanotechnology*, 18 (2007) 075708 (7pp).
- 13 N. Shah, D. Singh, S. Shah, A. Qureshi, N. L. Singh and K. P. Singh, *Bull. Mater. Sci.* 30 (5) (2007) 477-488.
- 14 H. Tang, *Mater. Lett.* 59 (2005) 1024.
- 15 CNR Rao, *Chemical Applications of IR Spectroscopy*, New York, Academic-Press (1963).
- 16 H. P. Wong B. C. Dave, F. Levioux, J Harreld, B. Dunn and L. F. Nazer, *J. Matter Chem.* 8 (1998) 1019-1027.