

International Journal of Physics and Applications

E-ISSN: 2664-7583
P-ISSN: 2664-7575
IJOS 2022; 4(1): 39-43
© 2022 IJPA
www.physicsjournal.in
Received: 16-01-2022
Accepted: 19-02-2022

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Synthesis and study of structural properties of Cu doped polypyridine-PVAc composite films

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DOI: <https://doi.org/10.33545/26647575.2022.v4.i1a.53>

Abstract

Polypyridine and their composites are attractive materials for the use in existing and emerging technologies because of their light weight and low cost. In the present paper, I focused on the structural properties of Cu-doped polypyridine polyvinyl acetate supported composite films, wherein polyvinyl acetate (PVAc) as the host matrix. Polypyridine-PVAc composite thin films were synthesized by chemical oxidative polymerization method with the solvent methanol and Copper chloride (CuCl) 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.

X-RD spectra shows the sharp peaks in all prepared samples represents the crystalline nature of material, which is due the phases of polypyridine and CuCl (JCPDS data file No. 01-077-2383). Crystalline nature of the material is seen from the scanning electron micrographs which also reflected in the XRD spectra. The IR spectra of all samples shows peaks at 1444.72, 1437.17 and 1456.27 cm^{-1} and second peak at 1595.38, 1595.87 and 1595.09 cm^{-1} may assigned to typical polypyridine ring vibration.

Keywords: Composites, polypyridine, X-RD, SEM, FTIR

1. Introduction

The conductive polymer can be made by filling an insulation polymer matrix with conducting particles such as metal flakes or metalized fibers, by chemical or electrochemical synthesis method to produced intrinsically conductive polymers ^[1]. 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 ^[2-3]. This paper deals with the synthesis and study of structural properties of all prepared Polypyridine-PVAc composite films. The structural study of all composite films was carried out through X-RD, SEM & FTIR techniques.

2. Experimental

2.1 Materials

Chemically polymerized polypyridine films were obtained at room temperature by oxidative polymerization by using CuCl as oxidant. The monomer pyridine (E. Merck, Germany), Cu (I) Cl (AR grade), polyvinyl acetate (PVAc) (AR grade) used as a starting materials for the preparation of polypyridine-PVAc composite films.

2.2 Preparation of sample

For the preparation of Cu doped composite films a mixed solution of PVAc and methanol (10:90) was prepared. In order to make the homogeneous solution the mixture is stirred for 3 to 4 hours and kept overnight. In prepared homogeneous solution 1 Mole CuCl (0.8595 gm) was added (This process was 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 CuCl, to form the conducting path, the concentration of CuCl was changed from 10 to 90 wt %. When monomer pyridine was added to the solution of PVAc, methanol and CuCl, a light green homogeneous solution was obtained. Glass plates (30 x 30 Cm^2) thoroughly clean with water and then with acetone, were used as a substrate. To achieve perfect leveling and uniformity in the thickness of the films the glass plate was leveled by using spirit level. Now the homogeneous solution was poured on the glass plate to prepared films of the composites.

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The whole assembly was placed in a dust free chamber maintained at constant temperature. In this way the Cu doped Polypyridine-PVAc composite films were prepared by isothermal evaporation technique [4]. After evaporation of solvent the thin films were formed, which were then washed with distilled water to remove the excess of CuCl.

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 CuK α ($\lambda = 1.5406\text{\AA}$). 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 Polypyridine-PVAc 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 VNIT, Nagpur. All samples were coated with platinum or 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, because it provides a lot of information. The FTIR spectrum of all Polypyridine-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.

3 Results and discussion

3.1 X-RD Spectra

The X-ray diffraction patterns of all PPy-PVAc composite films are shown in figure 1. In the present work XRD technique has been used to check the amorphous or crystalline nature of the samples. Sharp peaks in the samples represents the crystalline nature of material, which is due the phases of polypyridine and CuCl (JCPDS data file No. 01-077-2383). In all samples the peaks are observed at $2\theta = 16, 26,$ and 32° with d-values $5.41, 3.39$ and 2.75 \AA respectively, corresponding to (010), (200) and (020) planes due to the phases of polypyridine [5]. The peaks observed at $2\theta = 33$ and 47° are due to the CuCl phases corresponding to planes (200) and (220). The average crystallite size is estimated by using Scherrer's formula [6].

$$D = k\lambda/\beta\cos\theta \quad (1)$$

Where D is the crystallite size of particle, $\lambda = 1.54\text{ \AA}$ being the X-ray wave length of CuK α and k is the shape factor which can be assigned to a value of 0.89 if the sample is unknown, θ is diffraction angle at maximum intensity of peak and β is the full width at half maxima of angle of diffraction in radians. The diffraction pattern of all samples shows a number of peaks at different 2θ values. The analysis of these single peaks supports towards its crystalline nature.

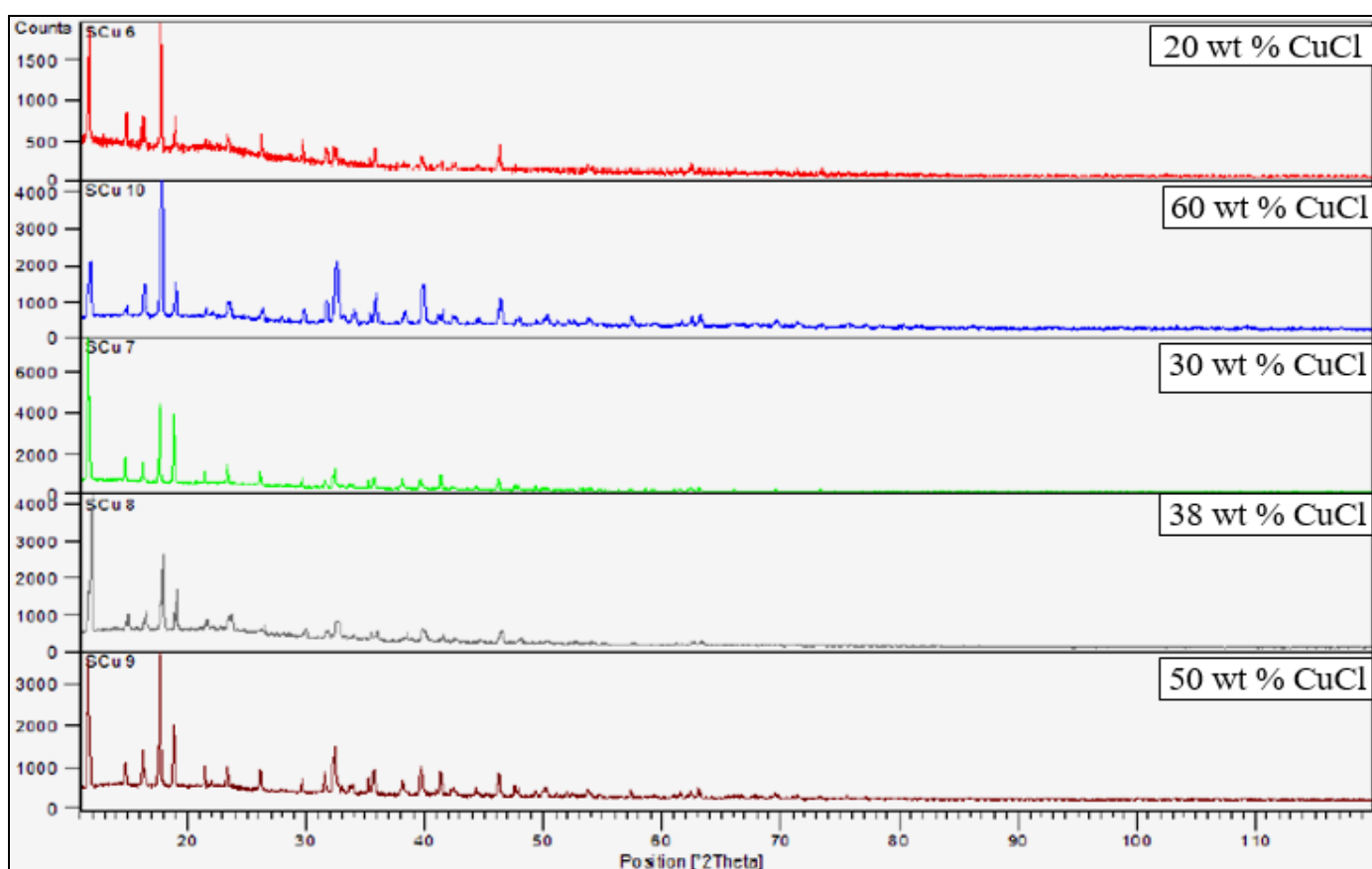


Fig 1: X-RD spectra for the samples

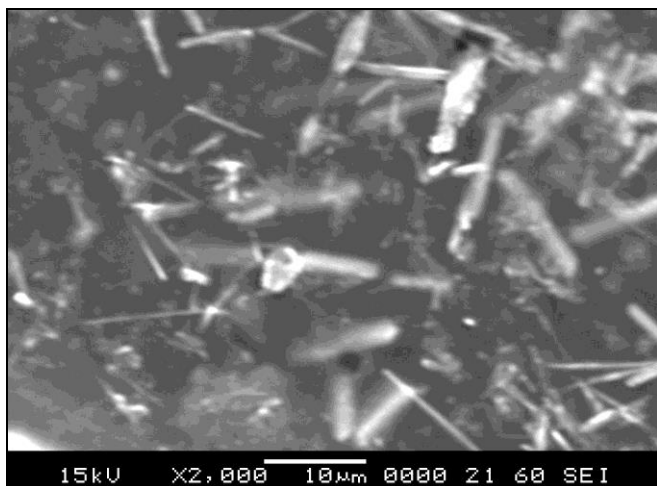
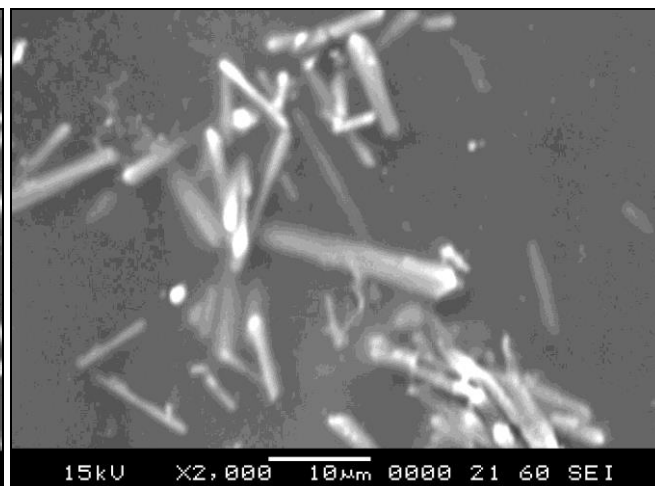
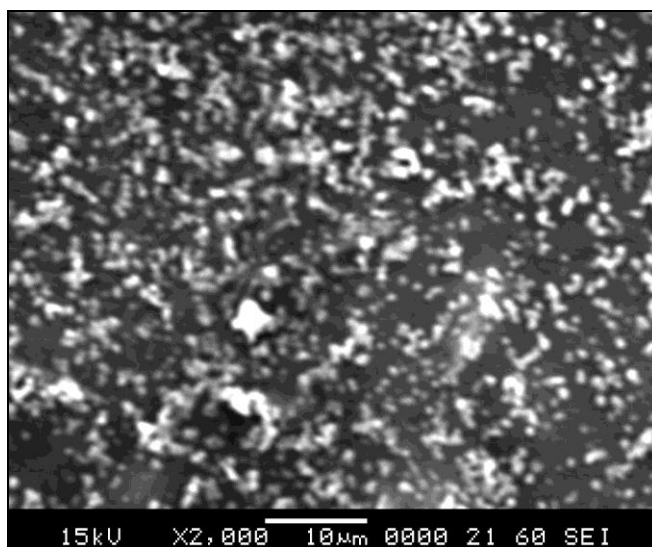
Table 1: Average crystallite size obtain from X-RD

Sample code	Max. peak intensity position 2θ	FWHM	$D=k\lambda/\beta\cos\theta$ (\AA)
SCu ₆	17.81	0.1224	22.66
SCu ₇	11.66	0.102	27.01
SCu ₈	11.95	0.1428	19.30
SCu ₉	17.69	0.1224	22.66

3.3 Scanning Electron Microscopy (SEM)

The surface morphology of Polypyridine-PVAc composite

films with different concentration of oxidizing agent was analyzed by SEM and the pictures are shown in figure 2(a), (b) and (c) respectively. It is seen that the crystals of CuCl amended in PPy-PVAc composite films. From SEM it is also clear the crystal density is less in figure 2(b) as compared to figures 2(a). The crystals size varies from ~ 3 to $5 \mu\text{m}$ in figure 2(a), while in figure 2(b) from ~ 1 to $2 \mu\text{m}$. However the more amorphous nature is seen in figure 2(c). The porous size varies from ~ 2 to $6 \mu\text{m}$.

**Fig 2a):** 30wt %**Fig 2b):** 38wt %**Fig 2c):** 50wt %**Fig 2 (a-c):** SEM photographs (CuCl as oxidizing agent)

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. In IR spectroscopy the energy associated with vibration of atoms in a molecule with respect to one another are quantized and absorption of electromagnetic radiation in the infrared region ($17 \lambda > 750 \mu\text{m}$, where λ is the wave length) gives rise to transition between these different vibrational states. Absorption results from coupling of vibration with the oscillating electric field of the infrared radiation, and this interaction can occur only when vibration produces an oscillating dipole moment. Since

vibration atoms are linked together by chemical bonds it is usual to refer to the vibrations as bonds deformations of which the simplest types of stretching and bending. The infrared radiation is defined by its wave number and the common absorption occurs in wave number range $4000\text{--}650 \text{ cm}^{-1}$ and for this reason IR spectra usually were recorded over this range [7].

Infrared spectra of Polypyridine-PVAc composite films are given in figure 3 and the corresponding absorption peak frequencies are tabulated in table 2. 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 the same though the

oxidizing agent is different and the oxidizing strength also different. An attempt is made to explain the structure of Polypyridine-PVAc composite with the help of infrared spectra.

The infrared spectra of sample SCu₇, SCu₈ and SCu₉ shows weak peak at 943.5, 944.73 and 943.17cm⁻¹ respectively which may be due to metal fillers in composite. In the aromatic C=C and C=N stretching region polypyridine exhibits a broad band at 1582 cm⁻¹ and sharp band at 1454 cm⁻¹. The IR spectra of all samples shows peaks at 1444.72,

1437.17 and 1456.27 cm⁻¹ and second peak at 1595.38, 1595.87 and 1595.09 cm⁻¹ for Cu₇, Cu₈ and Cu₉ samples respectively, may assigned to typical polypyridine ring vibration [8-9]. The bands at 1743.76, 1734.16 and 1745.75 cm⁻¹ for samples Cu₇, Cu₈ and Cu₉ may assigned to presence of PVAc. All samples shows two peaks at 2852 and 2920 cm⁻¹ may corresponds to symmetric and asymmetric C-H stretching. Thus the strong bands in the range 1745 to 943 cm⁻¹ confirmed the polymerization and conductive form of polymer composite.

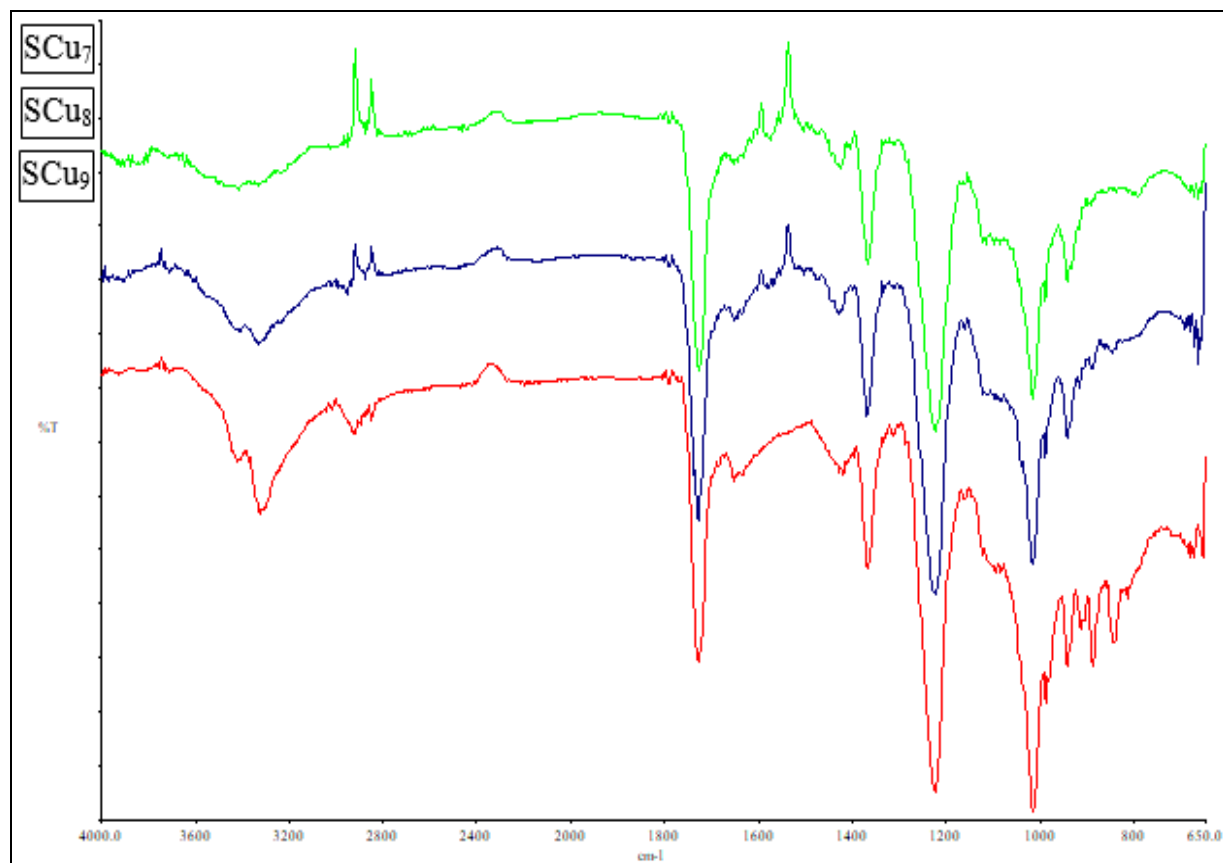


Fig 3: FTIR spectrums of PPy-PVAc composite films

Table 2: Experimental data from FTIR spectra

Sample code	Position of absorption maxima. cm ⁻¹											
	943.5	1017.06	1225.90	1317.49	1444.72	1595.38	1743.76	2323.32	2856.06	2909.96	3451.3	
Cu ₇ (30wt %)	943.5	1017.06	1225.90	1317.49	1444.72	1595.38	1743.76	2323.32	2856.06	2909.96	3451.3	
Cu ₈ (30wt %)	944.7	665.8	1018.51	1221.62	1372.2	1437.17	1595.87	1734.16	2322.17	2855.77	2924.16	3447.94
Cu ₉ (30wt %)	943.1	1016.56	1226.19	1373.0	1456.27	1595.09	1745.75	2324.37	2857.17	2928.18	3442.7	

Conclusion

Characteristics study of Polypyridine-PVAc composite films has been made by analyzing the films with XRD, SEM and FTIR. From the XRD spectra of PPy-PVAc composite films, it is observed that very sharp peaks are observed in the XRD spectra of all samples these are due to phases of CuCl. Sharp reflection peaks are also observed in all samples due to the phases of PPy and PVAc. Appearance of the sharp peaks indicates the crystalline nature of the composite material. The average crystalline size is estimated by using the Scherer's formula.

The surface morphology of Polypyridine-PVAc composite films with different concentration of oxidizing agent was analyzed by SEM. The crystalline nature of Polypyridine-PVAc composite films is due to dopant.

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 all investigated

films it is observed that the basic structure of the polymer composite is same though the oxidizing strength changing.

From the FTIR spectra it is observed that the sharp and medium peaks are seen in the range 678 to 1190 cm⁻¹ which may assigned to impurity and metal oxide present in the polymer composite material. The spectra of PPy-PVAc composite films display bands around 1606 and 1447 cm⁻¹ corresponding to aromatic C=C and C=N stretching region, which may associate to polypyridine ring vibrations. All samples shows two peaks at 2852 and 2920 cm⁻¹ which corresponds to symmetric and asymmetric C-H stretching. Thus the strong bands in the range 1015 to 1749 cm⁻¹ for all samples indicate the polymerization and conductive form of polymer composite.

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