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## Synthesis and characterization polyvinyl alcohol conjugates with some carboxylic acid and carbonyl compounds

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### Abstract

Synthesis and characterization of modified PVA polymer have been focused by using advance chemical methods and analytical methods, and its transition metal ions complexes was synthesized. Its characterization is carried out by using, FTIR, XRD, UV-visible spectroscopy and SEM. FTIR shows it is good arrangement with Literature values. UV bands are shifted towards the higher wavelength as the modification in PVA and complexation of modified PVAs, since polymer conjugates show red shift in formal peaks. Also absorbance is increases as modification and complexation. SEM shows solid state study of polymer conjugates also confirmed the semi-compatible nature of the polymer conjugates. XRD of MPVA and CMPVA shows the sharp reflections and diffuse scattering is characteristic of crystalline and amorphous phases of conventional semi-crystalline polymers.

**Keywords:** synthesis, characterization conjugates, carbonyl compounds, transition metal

### Introduction

A polymer is a large molecule composed of many repeated subunits, known as monomers. Because of their broad range of properties, both synthetic and natural polymers play an essential and ubiquitous role in everyday life. Majority of which are insulator, But some of the conjugated polymers show unique electronic properties derived from the presence of  $\pi$ -electrons which are delocalized over the long portion of the polymer chain. Prior to the early 1920's, chemists doubted the existence of molecules having molecular weight greater than a few thousand. Polymers, which distinguish them from metals, is their inability to carry electricity.

The insulating nature of the polymers is advantageous for many applications. For example, electrical wires are having the coating of insulating polymer, which is used to protect the short circuit. However during the last two decades; a new class of organic polymers with remarkable ability to conduct electrical current has been derived. This class of materials is called "synthetic metals". Some of these conductive materials are already under development for practical applications, such as rechargeable batteries, electrolytic capacitors, biosensors and chemical sensors [1-3]. Synthesis of PVA combs via matrix polymerization is reported [4]. Photo-emulsion copolymerization of vinyl acetate and vinyl pivalate were carried out without initiator at 0°C, and copolymers giving high molecular weight poly(vinyl alcohol) with various tacticities were obtained [5]. New hydrophilic PVA resins were prepared by an inverse suspension polymerization using epichlorohydrin as a cross linker [6]. A full-interpenetrating polymer network hydrogel based on poly (vinyl alcohol) /chitosan /poly (acrylic acid) by the simultaneous-IPN method was reported and characterized by FTIR and scanning electron microscopy [7].

Shivkumar V. Ghugare *et al.* [8] have studied Micro gels based on poly (vinyl alcohol) grafted with methacrylate side chains incorporating *N*-isopropyl acrylamide, NiPAAm monomer, which were prepared by water-in-water emulsion polymerization method. The influence of poly (vinyl alcohol) characteristics on the physical stability of encapsulated immobilization media for advanced wastewater treatment has been studied. Dielectric loss and A.C. conductivity have been studied for  $\gamma$ -irradiated polyvinyl alcohol doped with 30% by weight of  $\text{CrCl}_3$  [9].

Literature Survey demands improvement of different properties of various forms of PVA materials. In this investigation PVA has been chemically modified by using some

### Correspondence

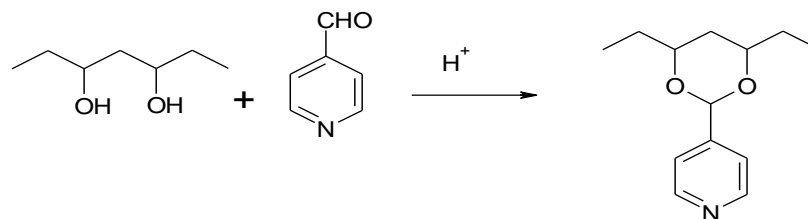
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advance chemical reactions. Modification of Poly vinyl alcohol is of special interest because, the introduction of these groups in polymer matrix, changes the physical properties, electrical conductivity, and many other properties of PVA. In the present research work, synthesis and characterization of modified PVA polymer have been focused due to their wide range of applications in various fields of human interest. In present work we have undertaken synthesis of modified polyvinyl alcohol materials by using, Modification of PVA using p-Dimethyl amino benzaldehyde (PDB), Modification of PVA using p-Formyl pyridine (PFP) Modification of PVA using p-formylbenzoic acid (PFB), Modification of PVA using p-formyl benzene sulfonic acid (PFS). And its characterization carried out by using, FTIR, XRD, UV-visible spectroscopy and SEM.

### Material and Methods

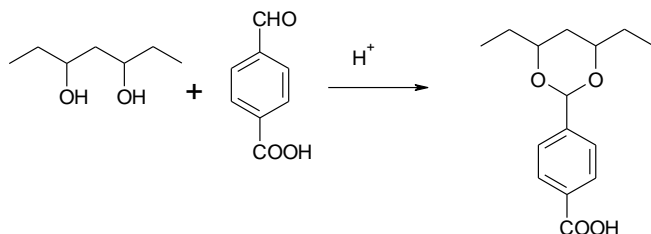
Synthesis and characterization of modified PVA polymer have been focused due to their wide range of applications in various fields of human interest. We have undertaken synthesis of modified polyvinyl alcohol by using,

- Modification of PVA using p-Dimethylaminobenzaldehyde (PDB)
- Modification of PVA using p-Formylpyridine (PFP)
- Modification of PVA using p-formylbenzoic acid (PFB)
- Modification of PVA using p-formylbenzene sulfonic acid (PFS)



### • Modification of PVA using p-formyl benzoic acid (PFB)

The amount of p-Formyl benzoic acid dissolved in DMF and then added to 10 % aqueous solution of PVA in presence of concentrated  $H_2SO_4$  as a catalyst. The reaction was carried out at  $90^\circ C$  for 2 hours. Then mixture was dilute with water and then 50 % sodium hydroxide solution was added to precipitate the product recrystallized with ethanol <sup>[2]</sup>. The product is act as a polyanion.

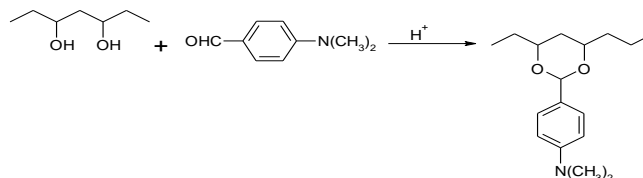


### • Modification of PVA using p-formylbenzene sulfonic acid (PFS)

The amount of p-Formyl benzene sulfonic acid dissolved in DMF and then added to 10 % aqueous solution of PVA in presence of conc.  $H_2SO_4$  as a catalyst. The reaction was carried out at  $180^\circ C$  for 1 hours. Then mixture was dilute with water and then 5 % sodium hydroxide solution was added to precipitate the product recrystallized with ethanol <sup>[2]</sup>. The product is act as a polyanion.

- Preparation of transition metal ions complexes of modified PVA
- Modification of PVA using p-Dimethylaminobenzaldehyde (PDB)

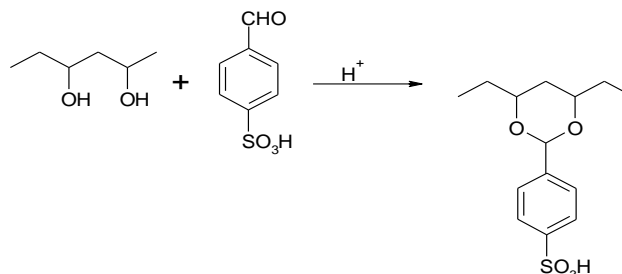
The amount of p- Dimethylaminobenzaldehyde dissolved in 60% sulfonic acid was added to 10 % aqueous solution of PVA. After the reaction was carried out at  $210^\circ C$  for 1 hour the mixture was dilute with water and then 5 % sodium carbonate solutions was added to precipitate the product. The product is act as a polycation.



### • Modification of PVA using p-Formylpyridine (PFP)

#### Procedure

The amount of p-Formylpyridine dissolved in 50% sulfonic acid was added to 10 % aqueous solution of PVA. After the reaction was carried out at  $200^\circ C$  for 1hours the mixture was dilute with water and then 10 % sodium carbonate solutions was added to precipitate the product. The product is act as a polycation.



Characterization of modified PVA has been largely based on the surface analysis techniques and conventional characterization methods developed for bulk materials. These include: XRD <sup>[10]</sup>, UV- Visible <sup>[11-12]</sup>, FT-IR <sup>[13]</sup> and SEM <sup>[14]</sup>.

### • Fourier Transform Infra-Red Spectroscopy

FTIR characterization of modified polyvinyl alcohol and complex modified polyvinyl alcohols is found to be important for investigation of polymer structure that provides information about the complexation and interactions between the various constituents in the polymeric films. Each type of bond has a different natural frequency of vibration, so the identification of an absorption peak in the vibration portion of the infrared region will give a specific type of bonding <sup>[15]</sup>. The FTIR spectra for modified polyvinyl alcohol and complex modified polyvinyl alcohols are shown in Figure 1 to 3 and observed vibrational frequencies are given in Table 1 to 3

**Table 1:** Observed vibrational frequencies of MPVA FTIR spectra

S NO.	Compounds	IR frequency in $\text{cm}^{-1}$
1.	PVA	3349, 2911, 1721, 1660, 1568, 1435, 1331, 1094, 918, 851.
2.	PDB	2999, 2510, 1655, 1568, 1440, 1330, 1100, 920, 750, 850, 1510
3.	PFP	3240, 2510, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1805.
4.	PFB	3340, 2910, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1290.
5.	PFS	3340, 2910, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 990.
6.	Literature values	3335, 2910, 1720, 1650, 1555, 1440, 1330, 1090, 900, 855.

**Table 2:** Observed vibrational frequencies of CPFP FTIR spectra

S NO.	Compounds	IR frequency in $\text{cm}^{-1}$
1.	PFP	3240, 2510, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1805.
2.	Fe(II)	3140, 2515, 1710, 1625, 1498, 1445, 1330, 1100, 920, 850, 810.
3.	Co(II)	3380, 2490, 1750, 1555, 1567, 1440, 1330, 1100, 970, 550, 493.
4.	Cu(II)	3290, 2610, 1825, 1655, 1578, 1447, 1100, 920, 850, 550.
5.	Zn(II)	3310, 2510, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 592.

**Table 3:** Observed vibrational frequencies of CPFB FTIR spectra

S NO.	Compounds	IR frequency in $\text{cm}^{-1}$
1.	PFB	3340, 2910, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1290.
2.	Fe(II)	3310, 3010, 1780, 1665, 1468, 1490, 1339, 1100, 990, 820.
3.	Co(II)	3040, 2790, 1790, 1655, 1568, 1440, 1335, 1190, 920, 850, 490.
4.	Cu(II)	3300, 2980, 1700, 1650, 1560, 1440, 1330, 1100, 940, 855, 555.
5.	Zn(II)	3350, 2900, 1800, 1655, 1568, 1520, 1335, 1150, 910, 840, 598.

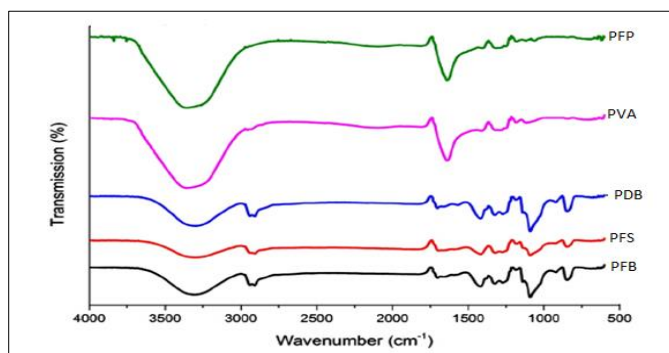
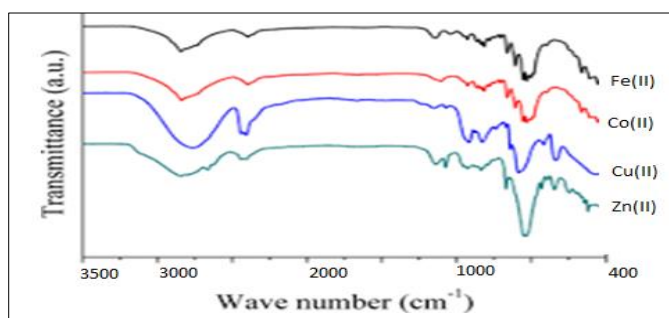
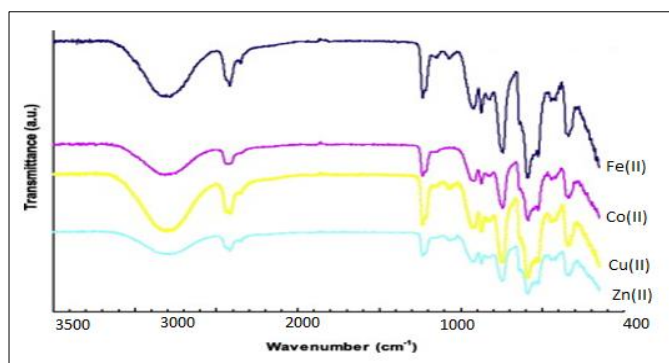
**Fig 1:** FTIR spectra of MPVA**Fig 2:** FTIR spectra of PFB Complexes**Fig 3:** FTIR spectra of PFP Complexes

Figure 1 to 3 showed the absorption peaks of PVA MPVA and CMPVA at different frequencies PVA absorb at  $3349\text{ cm}^{-1}$  (-OH, stretch),  $2911\text{ cm}^{-1}$  (-CH<sub>2</sub>, stretch),  $1660\text{ cm}^{-1}$  (C=C),  $1568\text{ cm}^{-1}$  (CH<sub>2</sub>, b),  $1435\text{ cm}^{-1}$  (CH-OH),  $918\text{ cm}^{-1}$  (C-C),  $851\text{ cm}^{-1}$  (CH<sub>2</sub>, b)  $\text{cm}^{-1}$  [18, 9]. Whereas modified PVA gives characterized peak at  $1510\text{ cm}^{-1}$ ,  $1805\text{ cm}^{-1}$ ,  $1290\text{ cm}^{-1}$  and  $990\text{ cm}^{-1}$  respectively for PDB, PFP, PFB And PFS. Also complexes of PFP with Fe(II), Co(II), Cu(II), Zn(II) gives peak at  $810$ ,  $493$ ,  $550$ ,  $592\text{ cm}^{-1}$ . And PFB complexes with Fe(II), Co(II), Cu(II), Zn(II) gives peak at  $820$ ,  $490$ ,  $550$ ,  $598\text{ cm}^{-1}$ . And it is good arrangement with Literature values [16-17].

### 3.3 UV-Visible spectroscopy

UV-Visible spectra of MPVA and CMPVA were recorded on Shimadzu UV-1800 spectrophotometer, polymer conjugates by placing an uncoated identical conducting glass substrate in the reference beam ranging from 200 to 800nm. A plot of absorption coefficient versus wavelength for all synthesized samples shown in Figure 4 to 5, Wavelength for maximum absorbance  $\lambda_{\text{max}}$  and corresponding optical band gap for all samples are presented in Table 4 to 6. Polymer conjugates have a conjugate system of double bonds on their backbone. The polymers have some of the conventional transition in the UV-visible region, such as  $\sigma\text{-}\sigma^*$ ,  $\Pi\text{-}\Pi^*$ ,  $n\text{-}\Pi^*$  etc. The  $\sigma\text{-}\sigma^*$  transition of conjugated double bonds are related to near UV regions around 200 nm, UV-visible spectra of the spectrum of pure PVA is characterized by an absorption edge at wavelength 277 nm. No absorption peaks are noticed at higher wavelengths. This absorption edge can be attributed for carbonyl groups conjugated with one ethylinic group [18-23]. These bands are shifted towards the higher wavelength as the modification in PVA and complexation of modified PVAs, the values associated with these transitions are shown in Table-4, 5 and 6. Since polymer conjugates show red shift in formal peaks. Also absorbance is increases as modification and complexation.

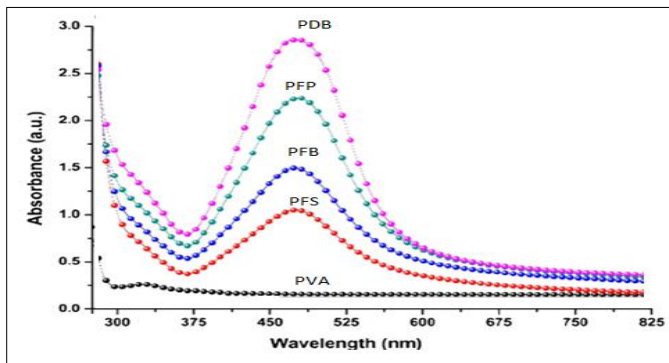


Fig 4: UV-Visible Spectra of pure PVA and MPVA

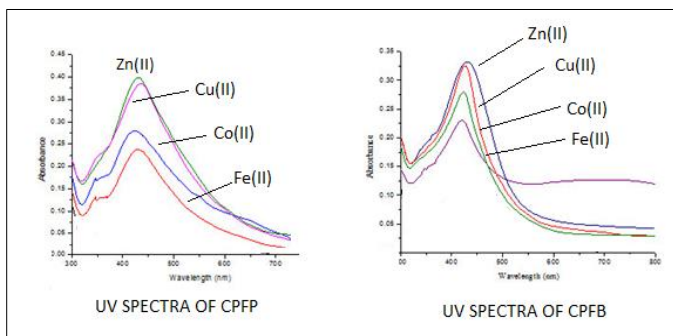


Fig 5: UV-Visible Spectra of CMPVA

Table 4: UV-Visible spectral data MPVA

Materials	$\lambda_{max}$ nm	Absorbance (au)
PVA	277	0.25
PDB	510	2.90
PFP	495	2.50
PFB	498	1.45
PFS	505	1.00

Table 5: UV-Visible spectral data of PFP complexes.

Materials	$\lambda_{max}$ nm	Absorbance (au)
PFP	495	2.50
Fe(II)	550	3.30
Co(II)	540	3.26
Cu(II)	525	3.20
Zn(II)	525	3.15

Table 6: UV-Visible spectral data of PFB complexes.

Materials	$\lambda_{max}$ nm	Absorbance (au)
PFB	498	1.45
Fe(II)	590	3.67
Co(II)	585	3.58
Cu(II)	563	2.87
Zn(II)	527	2.69

3.4 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is an important tool to investigate the surface and morphology of the polymer materials. By using it we can estimate the diameter, length, thickness, density, shape and orientation of the polymer materials. (SEM) photographs of MPVA and CMPVA are shown below.

Scanning electron microscopy (SEM) is a powerful technique to determine miscibility of polymers. The SEM photograph of pure PVA is shown in figure 6, it is observed that PVA has uniform surface and size varies from 1  $\mu$ m to 100  $\mu$ m in length. The uniformity of the dispersion of the modified PVA was examined through SEM and the corresponding micrographs are as shown in Figures-6. In PDB (b) and PFP (c), PFB (d) and PFS (d), PVA (a) was dispersed completely and showed single phase and in CMPVA films showed rough surface which can be observed in SEM. This may be due to high viscosity of PVA in CMPVA. The solid state study of polymer conjugates also confirmed the semi-compatible nature of the polymer conjugates [24].

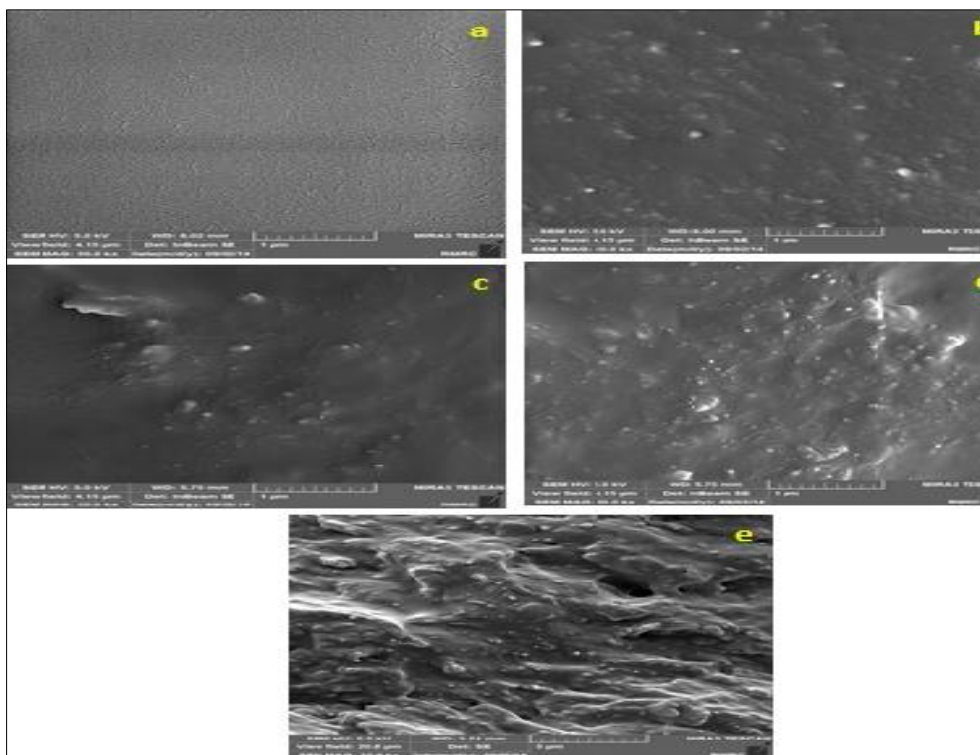


Fig 6: SEM image of Pure PVA and Modified of PVA

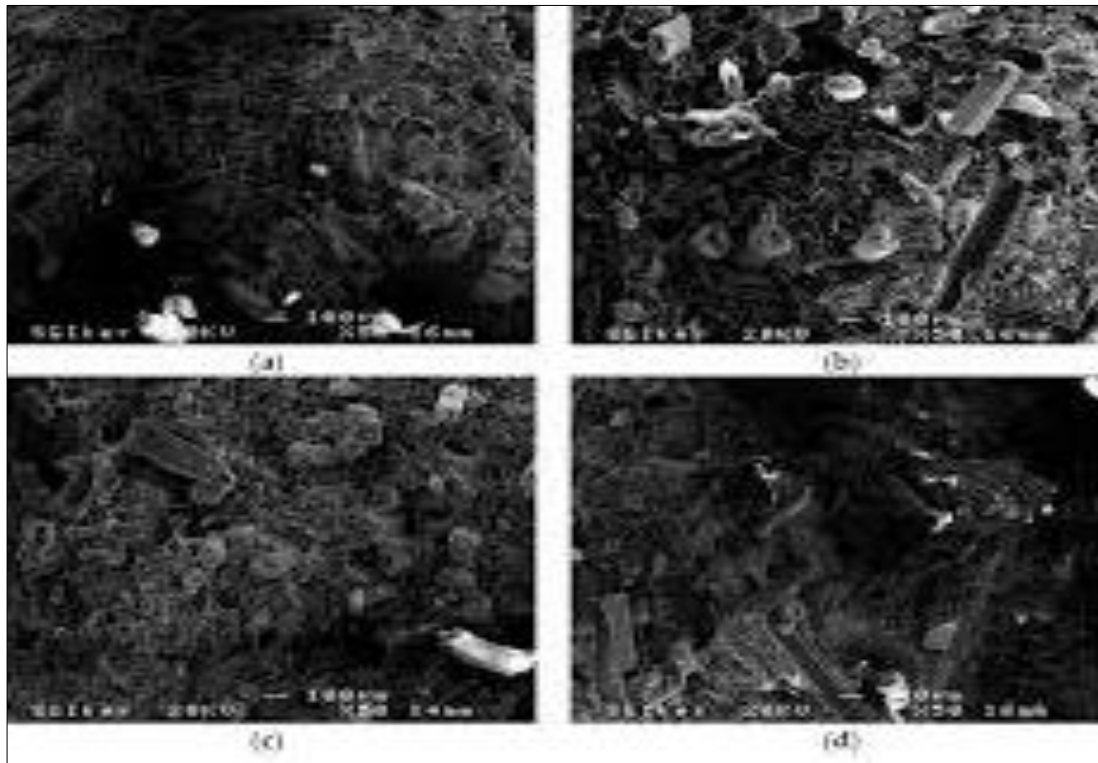


Fig 7: SEM image CPFP

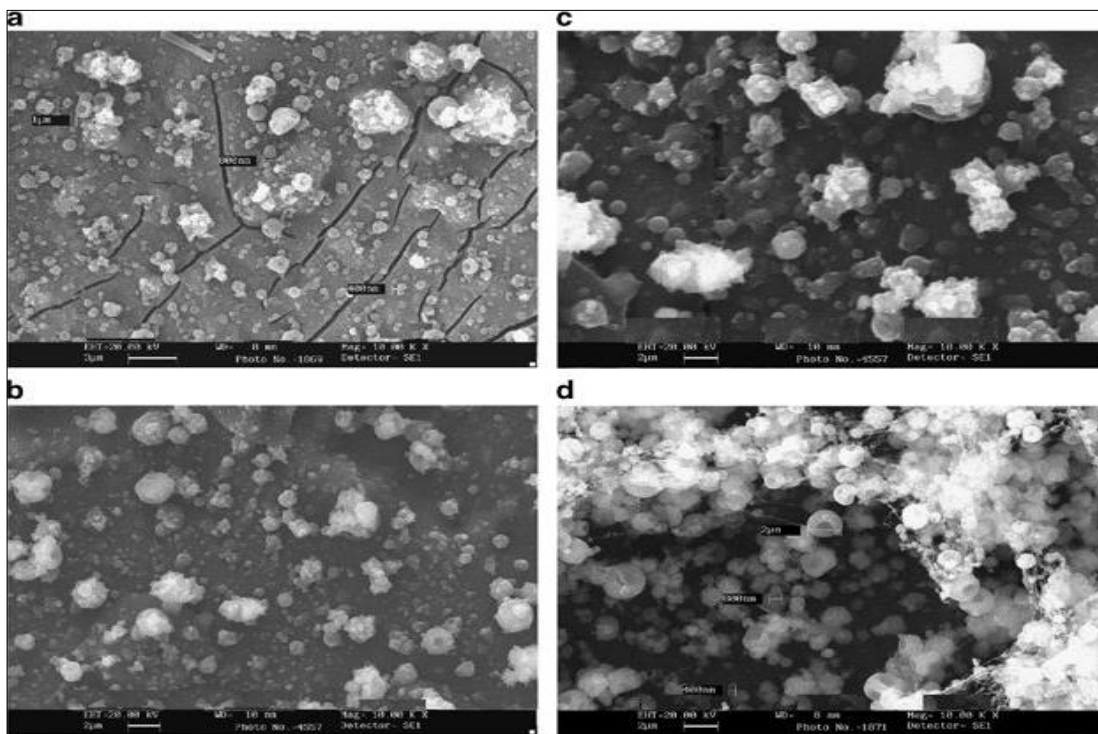


Fig 8: SEM image CPFB

The SEM photograph of CMPVA show that number of voids in the field and voids size are almost same over entire surface voids size are very small and varies from 1  $\mu\text{m}$  to 100  $\mu\text{m}$  [25-24].

### 3.5 X-Ray Diffraction (XRD)

The XRD profiles of pure PVA, MPVA and CMPVA are shown in Figure 9 to 10

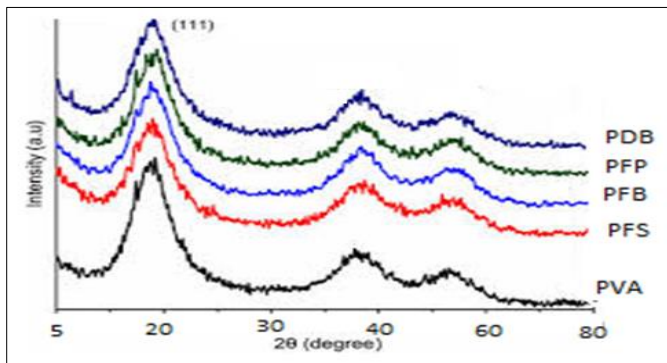


Fig 9: XRD Spectra of pure PVA and MPVA.

Figure.- 9 shows the x-ray diffraction of PVA and MPVA samples at room temperature in the scanning range  $5^\circ \leq 2\theta \leq 80^\circ$ . Spectrum of pure PVA shows an intense reflection peak at  $2\theta = 19.9^\circ$  diffused in the hallow amorphous region and was assigned to a mixture of (101) and (10 $\bar{1}$ ) reflections [19]. The appearance of sharp reflections and diffuse scattering is characteristic of crystalline and amorphous phases of conventional semi-crystalline polymers [27].

However, spectrum of PDB shows a broad amorphous halo with a scattered intensity, maximum corresponding to  $2\theta = 21.9^\circ$ . It reflects the absence of any diffraction lines, indicating the amorphous nature of PDB. It is known that glassy amorphous polymers are typically optically clear; showing a liquid-like x-ray pattern [28].

XRD patterns PFP and PFB of samples exhibited the characteristics of pure PVA, but with less intensity for the reflection peak. Thus, one can say that the semi-crystalline structure of PVA decreases upon modification. However, XRD pattern PFS shows an intense broad halo amorphous covering the positions of those found in homopolymers, for the semi-crystalline/amorphous nature, the non-crystallizing component could strongly modify the crystallization behavior of crystallizing component [29]. For MPVAs, compatibility between the amorphous components of both homopolymers is possible. Thus, it can be suggested that the crystal forms in PVA do not prevent the compatibility between amorphous regions of the two polymers.

XRD patterns exhibited strong diffraction peaks at  $26^\circ$ ,  $35^\circ$  and  $56^\circ$  indicating transition metal ions in the rutile phase and strong diffraction peaks at  $22^\circ$  and  $42^\circ$  indicating transition metal ions in the anatase phase. CMPVA shows characteristic broad peak for an orthorhombic lattice centered at  $19^\circ$  to  $22^\circ$  including semi crystalline nature of all CMPVA [30]. With addition of transition metal ions, intensity of this peak decreases, suggesting the decrease in degree of crystallinity of the complex [31]. This may be due to the disruption of the CMPVA crystalline structure by transition metal ions as suggested [32]. They are compared with JCPDS No. 88-1175, JCPDS No. 84-1286 and observed that the intensity of XRD pattern decreases as the amorphous nature increases with addition of metal ions. This amorphous nature result in greater ion diffusivity with high ionic conductivity, and can be expressed as amorphous polymers having flexible back bone [33].

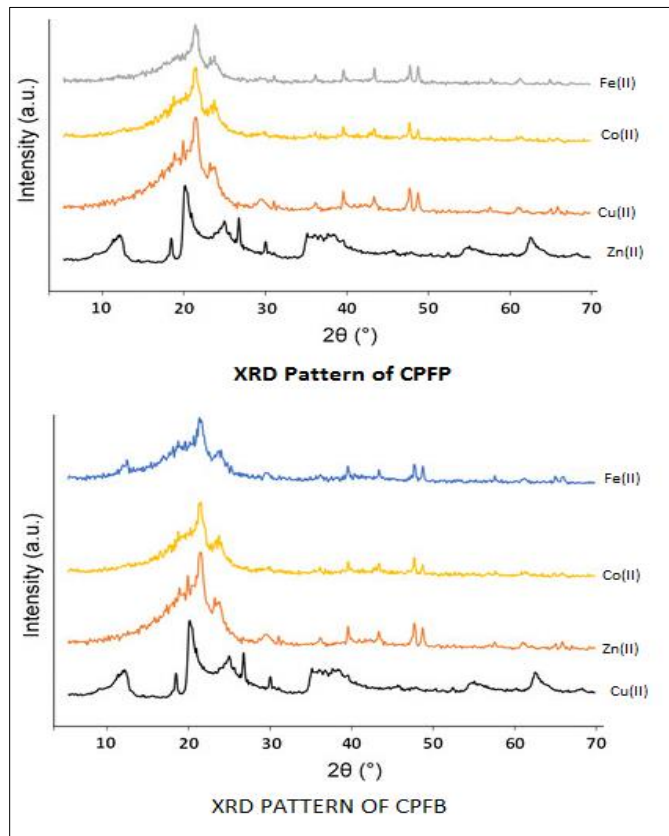


Fig 10: XRD Spectra of CMPVA

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