

Synthesis and Characterization of Complexes of Remodulated Polyvinyl Alcohol Conjugates

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Abstract: *The synthesis and characterization of complexes of remodulated polyvinyl alcohol conjugates was studied by using chemical method. Characterizations of RPVA were carried out by using FTIR, XRD. It showed that, for RPVAs, 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. Fourier transform infrared FTIR spectra of all polymer conjugates under investigation were recorded between 400 and 4000cm⁻¹.*

Keywords: *Remodulated Polyvinyl Alcohol, FTIR, XRD, RPVA and CRPVA*

1. INTRODUCTION

Polymer complexes have been given a great deal of attention in recent years [1-3]. Polyvinyl alcohol (ethanol homopolymer) which considered as moderate adhesive is a water – soluble resin. PVA is a polymer with exceptional properties such as water solubility, biodegradability, biocompatibility, non-toxicity and non-carcinogenicity that possesses the capability to form hydrogels by chemical or physical methods [4–6]. Its fields of applicability were widely broadened during the later years due to the development of medicine.

Poly (vinyl alcohols), (PVA) are widely used in polymer science fields because the advantages of PVA are water-soluble polymer, biodegradable polymer and low toxic [7-8]. The chemical modification has subsequently applied to improve the properties of macromolecules, leading to many applications of PVA, especially made in polymer hydrogel [9]. Hydrogels are three-dimensional networks of dispersed polymer chains in water that are held together by physical or chemical crosslink. They are generally made from hydrophilic polymers that are subsequently cross linked producing networks characterised by a high degree of swelling without dissolution and it was used in medical applications due to their high water content and hydrophilic nature.

Polymer which is Polyvinyl alcohol or known as PVA is a non-toxic, water soluble, bio compatible and biodegradable synthetic polymer have been widely used in biomedical field. PVA has been better fiber-forming and highly hydrophilic properties and its fibers have been commercialized since the 1950s [10]. Polymers have received much experimental attention, due to their unique properties, such as low density, ability to form intricate shapes, versatile electric properties and low manufacturing cost [11]. In the present research work, synthesis and characterizations of remodulated Polyvinyl Alcohol complexes with transition metal ions was carried out and its characterization using FTIR, and XRD was used

2. MATERIAL AND METHODS

All the chemicals used in this work were obtained from Merck. Following advance methods are used for remodulation of PVA

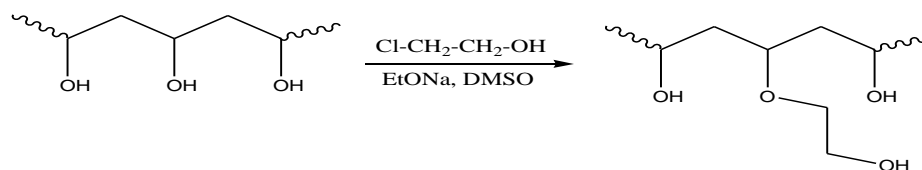
2.1. Hydroxyethylation of PVA with Chloroethanol

Chemical Required: Na metal, ethanol, anhydrous DMSO, chloroethanol

Procedure

In 200 ml ethanol the amount of 10 g of Na metal was dissolved. The excess of ethanol was evaporated in vaccum. The remaining sodium ethoxide was solubilized into 200 ml of anhydrous

DMSO under nitrogen, and 14 g of PVA was added. The mixture was stirred vigorously to give a gelatinous product. The residual alcohol was removed under vacuum. The resulting sodium polyvinyl alcoholate was dissolved in 200 ml DMSO and 26 ml of freshly distilled chloroethanol was added. The mixture was stirred 5 hours at 90°C temperature. The polymer solution was precipitated into methanol to give a fluorescent white solid (*Scheme -1*).



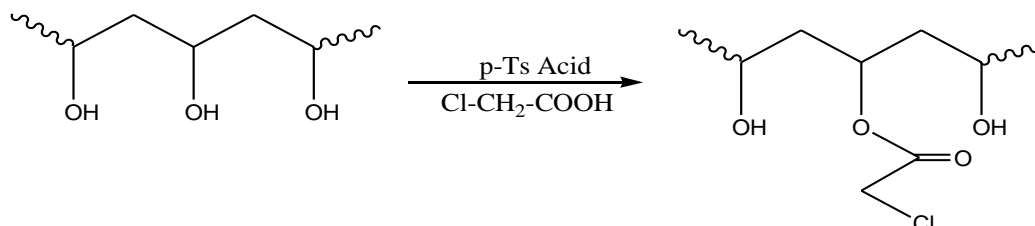
Scheme1. Hydroxyethylation of PVA with Chloroethanol

2.2. Chloroacetylation of PVA with Chloroacetic Acid

Chemical Required: PVA, para-toluenesulphonic acid, 1,2-dichloroethane, chloroacetic acid.

Procedure

40 g PVA and 8 ml para-toluenesulphonic acid were dissolved in 200 ml 1,2-dichloroethane at 110 °C. To this solution was added 70 ml of chloroacetic acid. The mixture was stirred at 90 °C for 1 hour. After cooling to room temperature, the polymer was precipitated by cold ethanol, dissolved in a solution of sodium carbonate in acetone and reprecipitated several times into ethanol (*Scheme -2*).



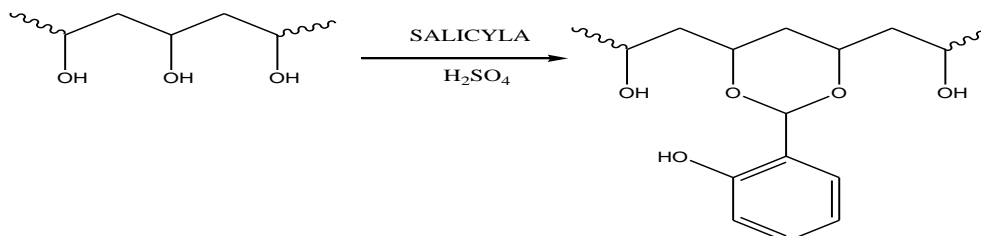
Scheme2. Chloroacetylation of PVA with Chloroacetic Acid

2.3. Acetalization of PVA with Salicylaldehyde

Chemicals: PVA, salicylaldehyde, 5% aqueous H₂SO₄, DMSO and methanol

Procedure

A mixture of 20 g PVA, 32 ml salicylaldehyde, and 20 ml 5% aqueous H₂SO₄ in 200 ml water was stirred at 60 °C for 4 hours. The precipitated Polymer was filtered and dissolved in DMSO. The polymer solution was reprecipitated by a large amount of methanol (*Scheme -3*).



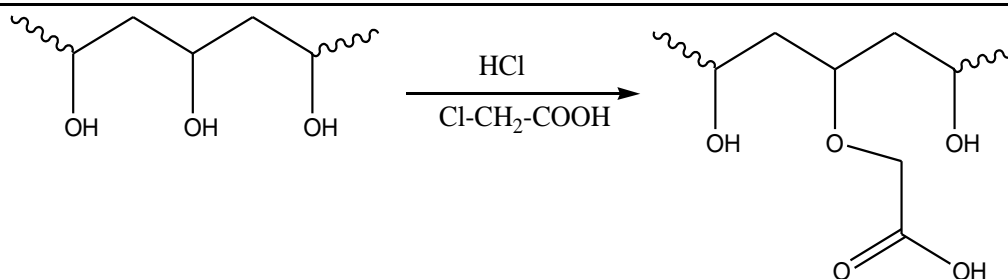
Scheme3. Acetalization of PVA with Salicylaldehyde

2.4. Carboxymethylation of polyvinyl alcohol with MCAA

Chemical Required: PVA, aqueous potassium hydroxide, monochloroacetic acid, 0.1 N hydrochloric acid, methanol

Procedure

The 20 gm PVA was dissolved in 100 ml of aqueous potassium hydroxide solution and heated in a water bath for half hour, 50 ml of MCAA was then added and the reaction mixture was stirred at 90°C for 1.5 hours. At the end of the reaction the mixture was acidified with 0.1 N hydrochloric acid. The product was precipitated with methanol. It was then dissolved in distilled water and reprecipitated from the solution using methanol. The process was repeated till the polymer became free of chloride ions (*Scheme.-4*).



Scheme4. Carboxymethylation of polyvinyl alcohol with MCAA

➤ Formation of Complexes of Remodulated Polyvinyl alcohols

For the Complexes of remodulated polyvinyl alcohol like carboxymethylated polyvinyl alcohol (CMPVA) and transition metal ions such as Cu (II), Co(II), Ni(II) and Zn(II) is used.

Cu(II), Co(II), Ni(II) and Zn(II) complexes of RPVA were prepared in the ratio 1:1 (metal: RPVA), by direct mixing of 0.5 mmol of metal salt, 0.5 mmol of ligand in the smallest quantity of DMSO. The mixture was refluxed for 1-5 h, then they form solid complexes. The latter were separated by filtration, washed with ethanol and finally with diethyl ether.

➤ Structural Characterization

Characterization of RPVA and CMPVA has been carried out by using XRD [12], ^1H NMR [13], FT-IR [14]. And some important properties like, magnetic properties [15] and fluorescence properties [16] was studied in order to understand the change in polymer matrix.

3. RESULT AND DISCUSSION

Fourier transform infrared FTIR spectra of all polymer conjugates under investigation were recorded on Shimadzu FTIR-8101A Spectrophotometer between 400 and 4000 cm^{-1} . XRD patterns of the doped modified PVA samples were recorded at using Phillips PW-1700, automatic X ray-diffractometer using Cu K α radiation of wavelength 1.544 \AA . UV-Visible spectra of MPVA were recorded on Shimadzu UV-1800 spectrophotometer, thin films by placing an uncoated identical conducting glass substrate in the reference beam in the range of 200 to 800 nm. A plot of absorption coefficient versus wavelength for all synthesized samples and Wavelength for maximum absorbance λ_{max} and corresponding optical band gap for all samples. The ^1H NMR spectra of polymer conjugates were taken in a DMSO using TMS as internal standard on Bruker Aavance-II 400 NMR spectrometer on 300 MHz and 75 MHz respectively. The chemical shifts measured are in PPM.

➤ Fourier Transform Infra-Red Spectroscopy

FTIR characterization of RPVA and CMPVA 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 [17]. The FTIR spectra for RPVA and CMPVA are shown in Figure 1 to 2 and observed vibrational frequencies are given in Table- 1

Table1. Observed vibrational frequencies of FTIR spectra

S NO.	Material	IR frequency in cm^{-1}
1.	PVA	3349, 2911, 1721, 1660, 1568, 1435, 1331, 1094, 918, 851.
2.	HEPVA	3240, 2510, 1655, 1568, 1440, 1330, 1100, 920, 850, 1052.
3.	CMPVA	3240, 2510, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1710.
4.	CAPCA	3340, 2910, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1765.
5.	ACPVA	3340, 2910, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1155.
6.	CMPVA-Cu(II)	3340, 2910, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1705, 460
7.	CMPVA-Co(II)	3340, 2910, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1705, 420
8.	CMPVA-Ni(II)	3340, 2910, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1705, 450
9.	CMPVA-Zn(II)	3340, 2910, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1705, 425

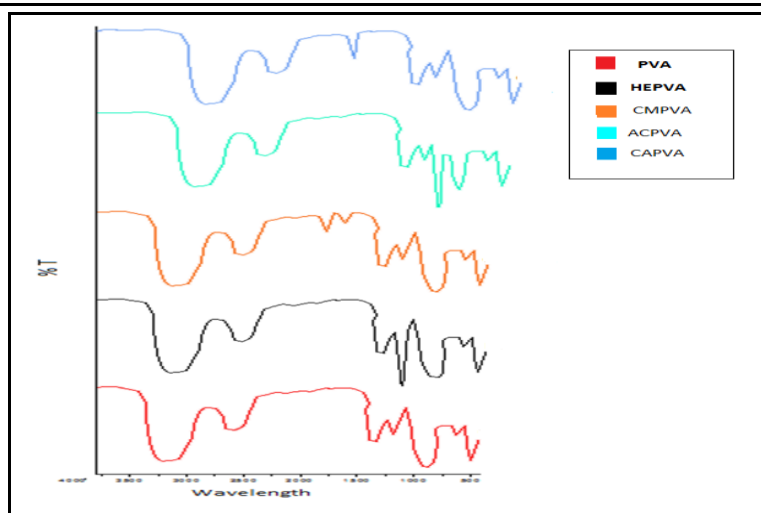


Figure1. FTIR spectra of RPVA

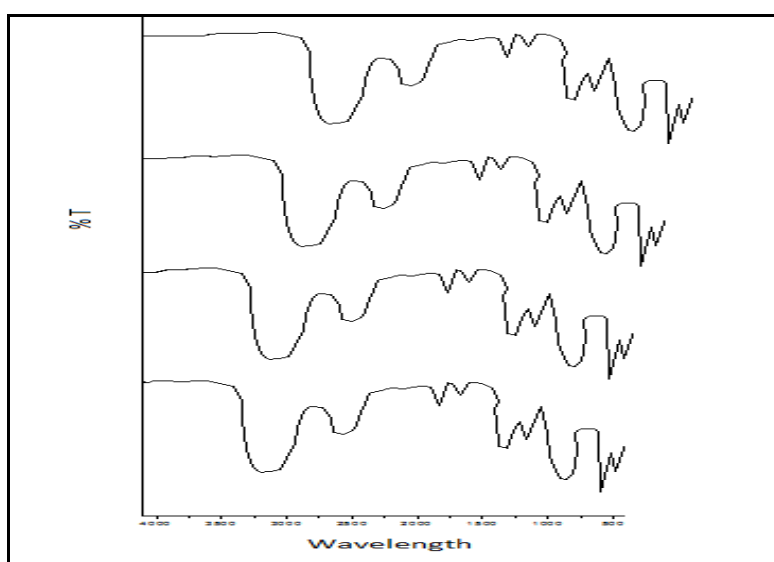


Figure2. FTIR spectra of CCMPVA

➤ Nuclear Magnetic Spectroscopy (¹H NMR Study)

¹H NMR gives the information about the type of protons present in the polymer matrix. The ¹H NMR spectra of pure PVA, RPVA and CCMPVA as shown below,

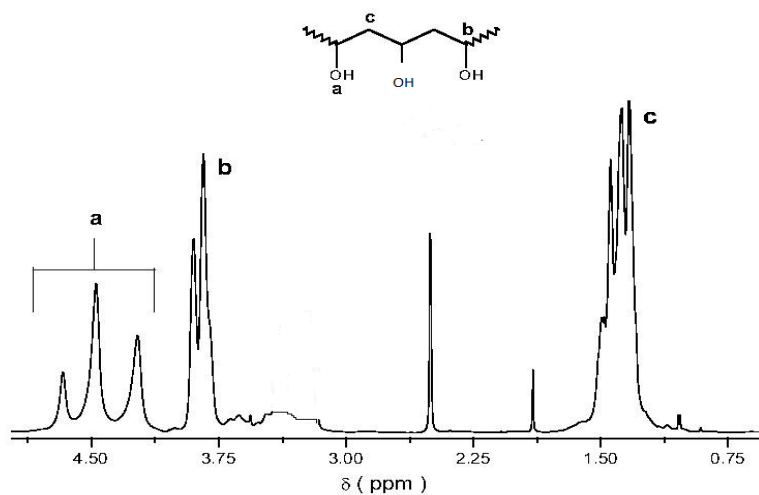


Figure3. NMR spectra of PVA

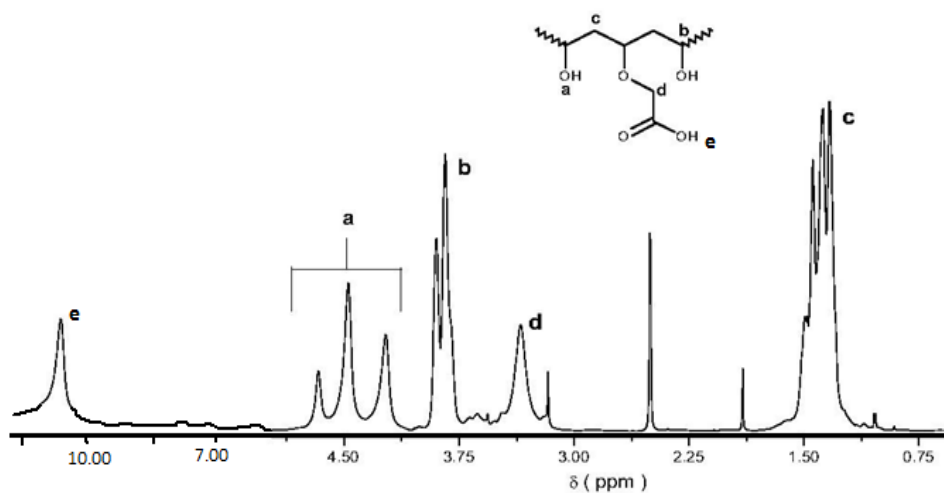


Figure4. NMR spectra of CMPVA

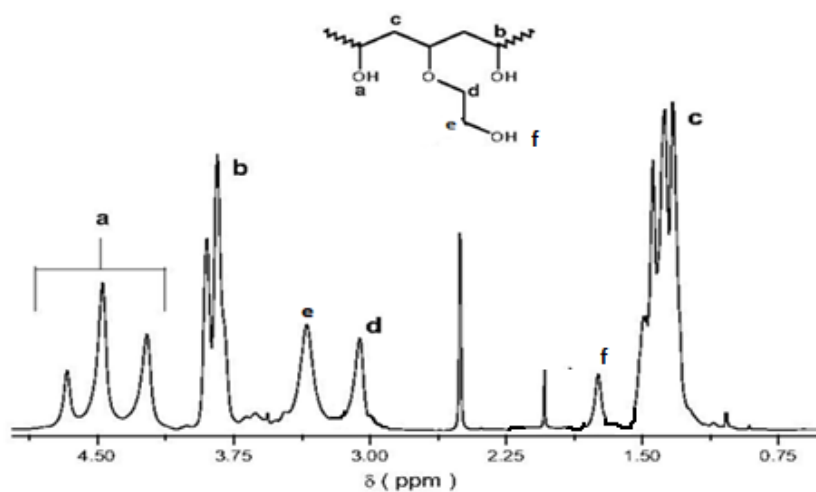


Figure5. NMR spectra of HEPVA

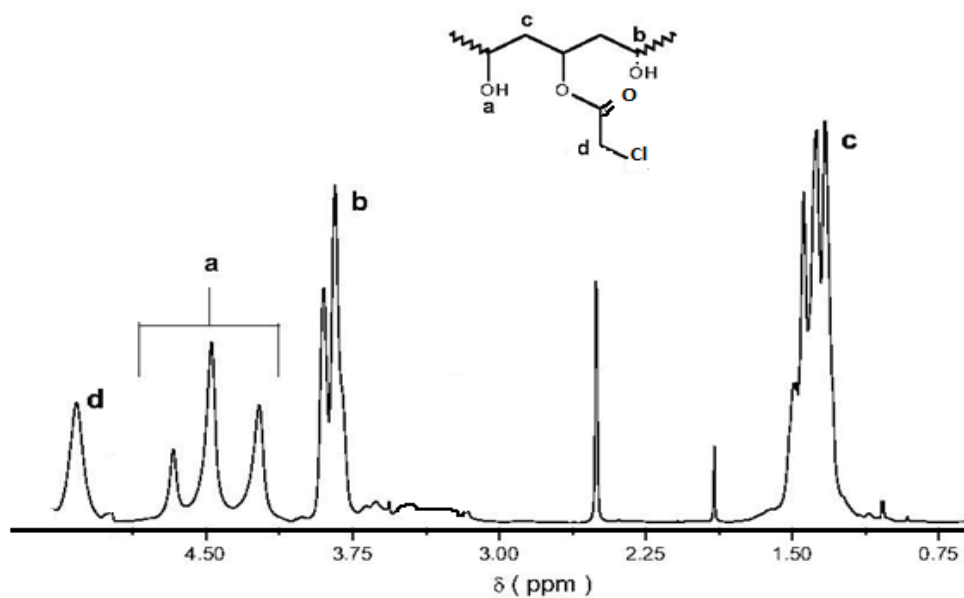


Figure6. NMR spectra of CAPVA

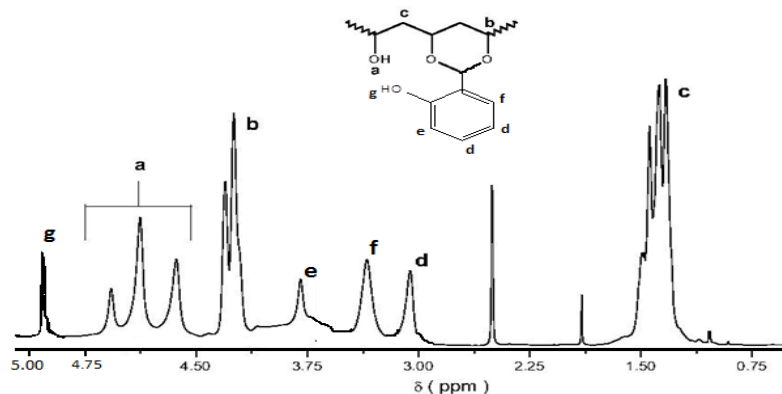


Figure7. NMR spectra of ACPVA

In CMPVA signal showed at 4.50 ppm (labelled a) was attributed to hydroxyl proton triads of *mm*, *mr*, *rr* from high to low frequency, whilst the signals labeled b and c were ascribed to the PVA polymer backbone (methine and methylene protons respectively). The signal at 3.50 ppm and signal at 10.5 ppm was attributed to the carboxymethyl methylene protons and carboxylic acid proton respectively.

HEPVA shows the signal at 4.51 ppm (labeled a) were attributed to hydroxyl proton triads of *mm*, *mr*, *rr* from high to low frequency, whilst the signal labeled b (3.80) and c (1.45) were ascribed to the PVA polymer backbone (methine and methylene protons respectively). The signals at 3.50 ppm, 3.12 ppm and 1.75 ppm were attributed to the chloroethylene methylene protons and hydroxyl proton respectively.

ACPVA shows the signal at 4.65 ppm (labeled a) were attributed to hydroxyl proton triads of *mm*, *mr*, *rr* from high to low frequency, whilst the signal labeled b (4.25) and c (1.40) were ascribed to the PVA polymer backbone (methine and methylene protons respectively). The signal at 3.80, 3.50, 3.20 and 4.95 ppm was attributed to the aromatic methylene and hydroxyl protons respectively.

CAPVA shows the signal at 4.50 ppm (labeled a) were attributed to hydroxyl proton triads of *mm*, *mr*, *rr* from high to low frequency, whilst the signal labeled b (3.80) and c (1.45) were ascribed to the PVA polymer backbone (methine and methylene protons respectively). The signal at 5.10 ppm was attributed to the chloroacetic methylene protons. Unfortunately there is no relevant data in literature to confirm this.

The signals at 3.16, 2.48 and 1.89 ppm were attributable to the following solvent contaminants methanol, DMSO and acetic acid respectively.

The NMR spectrum of CCMPVA clearly indicates that the chemical shift values are going to downfield. The signal at 4.50 ppm were attributed to hydroxyl proton triads of *mm*, *mr*, *rr* from high to low frequency shifted to 4.25, 4.20, 4.10, 4.05 for CMPVA-Cu(II), CMPVA-Co(II), CMPVA-Ni(II) and CMPVA-Zn(II) respectively. Whilst the signal labeled b and c were ascribed to the PVA polymer backbone (methine and methylene protons respectively) also shifted to downfield. The signal at 3.50 ppm was attributed to the carboxymethyl methylene protons also shifted.

➤ X-Ray Diffraction (XRD)

The XRD profiles of pure PVA, RPVA and CCMPVA with transition metal ions are shown in Figure 8 and 9.

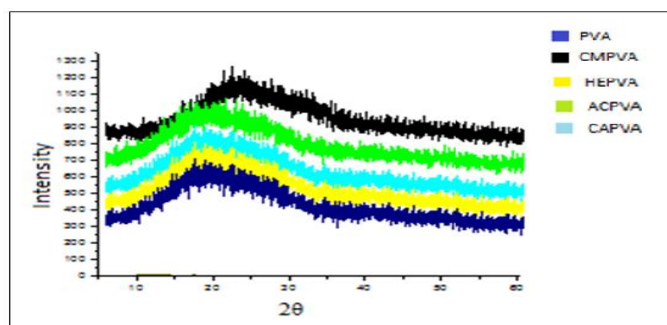


Figure8. XRD Spectra of pure PVA and RPVA

Figure.8 shows the x-ray diffraction of PVA and RPVA samples at room temperature in the scanning range $6^\circ \leq 2\theta \leq 60^\circ$. 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 [18]. The appearance of sharp reflections and diffuse scattering is characteristic of crystalline and amorphous phases of conventional semi-crystalline polymers [19]. However, spectrum of CMPVA shows a broad amorphous halo with a scattered intensity, maximum corresponding to $2\theta = 22^\circ$. It reflects the absence of any diffraction lines, indicating the amorphous nature of CMPVA. It is known that glassy amorphous polymers are typically optically clear; showing a liquid-like x-ray pattern [19]. XRD patterns HEPVA and CAPVA 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 ACPVA 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 [20]. For RPVAs, 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 25° , 36° and 55° indicating transition metal ions in the rutile phase and strong diffraction peaks at 22° and 42° indicating transition metal ions in the anatase phase. CCMPVA shows characteristic broad peak for an orthorhombic lattice centered at 19° to 22° including semi crystalline nature of all CCMPVA [21]. With addition of transition metal ions, intensity of this peak decreases, suggesting the decrease in degree of crystallinity of the complex [22]. This may be due to the disruption of the CMPVA crystalline structure by transition metal ions as suggested [23].

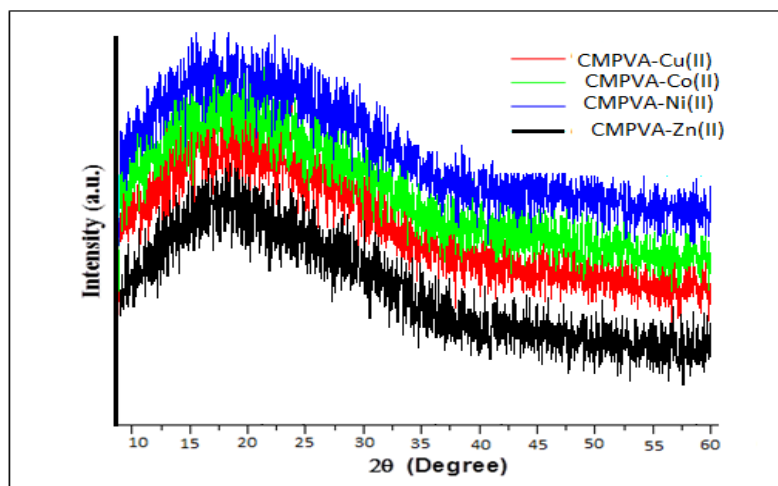


Figure9. XRD Spectra of CCMPVA

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