

Synthesis and Spectral Study of Doped Modified Cationic Polymer Conjugates Using Chemical Methods

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Abstract: *The synthesis and characterization of doped modified polyvinyl alcohol conjugates was studied by using casting method. Characterizations of DMPVA were carried out by using FTIR, ¹HNMR, XRD. It showed that, for DMPVA amorphous nature result in greater ion diffusivity with high ionic conductivity, and can be expressed as amorphous polymers having flexible back bone. Fourier transform infrared FTIR spectra of all polymer conjugates under investigation were recorded between 400 and 4000cm⁻¹. ¹H NMR gives the information about the various types of protons present in the polymer conjugates.*

Keywords: *Polyvinyl Alcohol, FTIR, ¹HNMR, XRD, MPVA and DMPVA,*

1. INTRODUCTION

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 [1-2]. The chemical modification has subsequently applied to improve the properties of macromolecules, leading to many applications of PVA, especially made in polymer hydrogel [3]. 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 characterized 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 [4]. 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. Literature Survey reveals that the demands improvement of different properties of various form of MPVA materials. In the present research work, synthesis of Doped modified Polyvinyl Alcohol was carried out and its characterization using FTIR, ¹HNMR and XRD was used

2. MATERIAL AND METHODS

All the chemicals used in this work were obtained from Merck.

Hydroxyethylated polyvinyl alcohol (HEPVA) and carboxymethylated polyvinyl alcohol (CMPVA) were used as a matrix polymeric material in this research with high purity. The aqueous solutions of these HEPVA and CMPVA were prepared by dissolving HEPVA and

CMPVA in a methanol and stirred by magnetic stirrer for about one hour until HEPVA and CMPVA were completely dissolved.

La (III), *Pr (III)*, *Nd (III)* and *Sm (III)* lanthanide metal salts (oxide) were dissolved in methanol. Appropriate mixtures of MPVAs and lanthanide metal salts solutions were mixed with stirring by magnetic stirrer for about one hour at 90 °C. The solution was poured into flat glass. Homogenous films were obtained after drying the solution in an oven for 24 hours. Samples of thin films of thickness 1 mm were measured within an accuracy (+ 0.01 mm) by a micrometer[5]. Characterization doped Modified PVA was carried by using FTIR, XRD, ¹H NMR, spectroscopy, in order to understand the change in polymer matrix.

Fourier transform infrared FTIR spectra of all polymer conjugates under investigation were recorded on Shimadzu FTIR-8101A Spectrophotometer between 400 and 4000cm⁻¹. XRD patterns of the doped modified PVA samples were recorded at using Phillips PW-1700, automatic X-ray-diffractometer using CuK α radiation of wavelength 1.544Å⁰. 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 800nm. A plot of absorption coefficient verses 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 BrukerAuaance-II 400 NMR spectrometer on 300 MHz and 75 MHz respectively. The chemical shifts measured are in PPM.

3. RESULTS AND DISCUSSIONS

Doped modified PVA is then characterized by using various techniques are as follows,

3.1. Characterization Modified PVA by Using FTIR

FTIR spectroscopy is an important 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 [6]. The FTIR spectra for modified polyvinyl alcohol are shown in *Figure-1* and observed vibrational frequencies are enclosed in *Table-1*

Table 1. The observed vibrational frequencies on spectra.

S NO.	Compounds	IR frequency in cm ⁻¹
1.	PVA	3349, 2911, 1721, 1660, 1568, 1435, 1331, 1094, 918, 851.
2.	CMPVA-La(III)	3340, 2910, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1705, 552
3.	CMPVA-Pr(III)	3340, 2910, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1705, 548
4.	CMPVA-Nd(III)	3340, 2910, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1705, 549
5.	CMPVA-Sm(III)	3340, 2910, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1705, 551
6.	HEPVA-La(III)	3340, 2910, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1050, 553
7.	HEPVA-Pr(III)	3340, 2910, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1050, 547
8.	HEPVA-Nd(III)	3340, 2910, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1050, 550
9.	HEPVA-Sm(III)	3340, 2910, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1050, 552
10.	<i>Literature values</i>	3335, 2910, 1720, 1650, 1555, 1440, 1330, 1090, 900, 855.

The spectrum of doped HEPVA in comparison with the spectrum of HEPVA is shown in figure -2. Some differences are visible in the spectrum of the polymer conjugates. The absorption band at 3240 cm^{-1} shifted to 3340 cm^{-1} and became broader. The absorption peaks of La (III)-HEPVA are at 3340 cm^{-1} due to O-H stretching and at 2910 cm^{-1} due to CH stretching. The characteristic absorption of the La (III)-HEPVA is the band at 553 cm^{-1} , which is assigned to the stretching vibration of metal ion linkage, and other bands observed at 1655 cm^{-1} (C=C), 1568 cm^{-1} (CH_2 , b), 1440 cm^{-1} (CH-OH), 920 cm^{-1} (C-C), $850(\text{CH}_2, \text{b})\text{ cm}^{-1}$ [7,8].

Absorption peaks of Pr (III)-HEPVA are observed at 3340 cm^{-1} due to O-H stretching and at 2910 cm^{-1} due to CH stretching. The characteristic absorption band of the Pr (III)-HEPVA is observed at 547 cm^{-1} , which is assigned to the stretching vibration of metal ion linkage with HEPVA, and other bands observed at 1655 cm^{-1} (C=C), 1568 cm^{-1} (CH_2 , b), 1440 cm^{-1} (CH-OH), 920 cm^{-1} (C-C), $850(\text{CH}_2, \text{b})\text{ cm}^{-1}$ [7,8].

The absorption peaks of Nd (III)-HEPVA are at 3340 cm^{-1} due to O-H stretching and at 2910 cm^{-1} due to CH stretching. The characteristic absorption band of the Pr (III)-HEPVA is observed at 550 cm^{-1} , which is assigned to the stretching vibration of metal ion linkage, and other bands observed at 1655 cm^{-1} (C=C), 1568 cm^{-1} (CH_2 , b), 1440 cm^{-1} (CH-OH), 920 cm^{-1} (C-C), $850(\text{CH}_2, \text{b})\text{ cm}^{-1}$ [7,8].

The absorption peaks of Sm (III)-HEPVA are at 3340 cm^{-1} due to O-H stretching and at 2910 cm^{-1} due to CH stretching. The characteristic absorption band of the Sm (III)-HEPVA is observed at 552 cm^{-1} , which is assigned to the stretching vibration of metal ion linkage (-M-O-), and other bands observed at 1655 cm^{-1} (C=C), 1568 cm^{-1} (CH_2 , b), 1440 cm^{-1} (CH-OH), 920 cm^{-1} (C-C), $850(\text{CH}_2, \text{b})\text{ cm}^{-1}$ [7,8].

Figure-1 presented the spectrum of doped CMPVA in comparison with the spectrum of CMPVA. Some differences are visible in the spectrum of the polymer conjugates. The absorption band at 3240 cm^{-1} shifted to 3340 cm^{-1} and became broader. The absorption peaks of La (III)-CMPVA are at 3340 cm^{-1} due to O-H stretching and at 2910 cm^{-1} due to CH stretching. The characteristic absorption band of the La (III)-CMPVA is observed at 552 cm^{-1} , which is assigned to the stretching vibration of metal ion linkage, and other bands observed at 7105 cm^{-1} (C=O), 1655 cm^{-1} (C=C), 1568 cm^{-1} (CH_2 , b), 1440 cm^{-1} (CH-OH), 920 cm^{-1} (C-C), $850(\text{CH}_2, \text{b})\text{ cm}^{-1}$ [9,8].

Characteristic absorption peaks of Pr (III)-CMPVA are at 3340 cm^{-1} due to O-H stretching and at 2910 cm^{-1} due to CH stretching. The absorption band of the Pr (III)-CMPVA is observed at 548 cm^{-1} , which is assigned to the stretching vibration of metal ion linkage, and other bands observed at 7105 cm^{-1} (C=O), 1655 cm^{-1} (C=C), 1568 cm^{-1} (CH_2 , b), 1440 cm^{-1} (CH-OH), 920 cm^{-1} (C-C), $850(\text{CH}_2, \text{b})\text{ cm}^{-1}$ [8,9].

Absorption peaks of Nd (III)-CMPVA are at 3340 cm^{-1} due to O-H stretching and at 2910 cm^{-1} due to CH stretching. The characteristic absorption band of the Nd (III)-CMPVA is observed at 549 cm^{-1} , which is assigned to the stretching vibration of metal ion linkage, and other bands observed at 7105 cm^{-1} (C=O), 1655 cm^{-1} (C=C), 1568 cm^{-1} (CH_2 , b), 1440 cm^{-1} (CH-OH), 920 cm^{-1} (C-C), $850(\text{CH}_2, \text{b})\text{ cm}^{-1}$ [8,9].

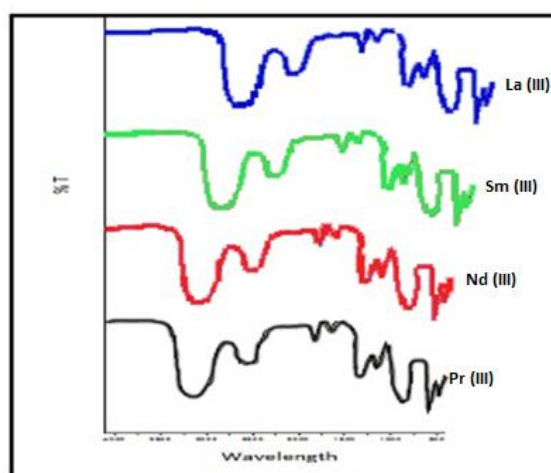


Figure1. FTIR spectra of doped CMPVA

Characteristic absorption peaks of Sm (III)-CMPVA are at 3340 cm^{-1} due to O-H stretching and at 2910 cm^{-1} due to CH stretching. The characteristic absorption band of the Sm(III)-CMPVA is observed at 551 cm^{-1} , which is assigned to the stretching vibration of metal ion linkage, and other band observed at 7105 cm^{-1} (C=O), 1655 cm^{-1} (C=C), 1568 cm^{-1} (CH₂, b), 1440 cm^{-1} (CH-OH), 920 cm^{-1} (C-C), $850(\text{CH}_2, \text{b})\text{ cm}^{-1}$ [8,9].

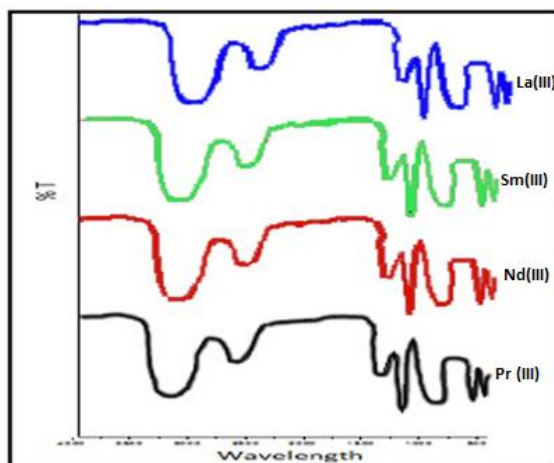


Figure 2. FTIR spectra of doped HEPVA

3.2. Characterization Modified PVA by using XRD

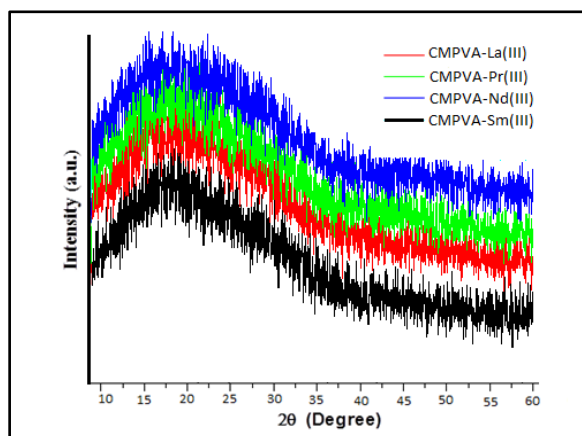


Figure 3. XRD Spectra of doped CMPVA.

XRD patterns exhibited strong diffraction peaks at 25° , 36° and 55° indicating lanthanide metal ions in the rutile phase and strong diffraction peaks at 22° and 42° indicating lanthanide metal ions in the anatase phase. Doped CMPVA shows characteristic broad peak for an orthorhombic lattice centered at 19° to 22° including semi crystalline nature of all doped CMPVA [10]. With addition of lanthanide metal ions, intensity of this peak decreases, suggesting the decrease in degree of crystallinity of the complex [11]. This may be due to the disruption of the CMPVA crystalline structure by lanthanide metal ions as suggested [12]. 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 dopant. This amorphous nature result in greater ion diffusivity with high ionic conductivity, and can be expressed as amorphous polymers having flexible back bone [13-16] (Fig.-3).

XRD patterns exhibited strong diffraction peaks at 24° , 34° and 55° indicating lanthanide metal ions in the rutile phase and strong diffraction peaks at 21° and 40° indicating lanthanide metal ions in the anatase phase. Doped HEPVA shows characteristics broad peak for an orthorhombic lattice centered at 20° to 22° including semi crystalline nature of all doped HEPVA. With addition of lanthanide metal ions, intensity of this peak decreases suggesting the decrease in degree of crystallinity of the complex. This may be due to the disruption of the HEPVA crystalline structure by lanthanide metal ions as suggested. It is observed that the intensity of XRD pattern decreases

as the amorphous nature increases with addition of dopant. This amorphous nature results in greater ion diffusivity with high ionic conductivity, and can be expressed as amorphous polymers having flexible back bone (Fig-4).

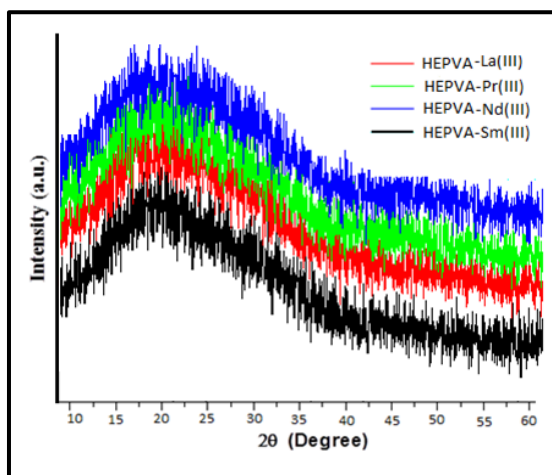


Figure 4. XRD Spectra of doped HEPVA.

3.3. Characterization Doped modified PVA by using ^1H NMR

^1H NMR gives the information about the type of protons present in the polymer conjugates. The NMR spectrum of doped CMPVA shows in Figure -5. It clearly indicates that the chemical shift values go to downfield. The signal at 4.50 ppm (labelled a) 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-La(III), CMPVA-Pr(III), CMPVA-Nd(III) and CMPVA-Sm(III) respectively. While the signals 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.

The NMR spectrum of doped HEPVA shows in Figure 6. It clearly indicates that the chemical shift values go to downfield. While the signals labeled b (3.80) and c (1.45) were ascribed to the PVA polymer backbone (methine and methylene protons respectively) also shifted to downfield. The signal at 3.12 ppm was attributed to the carboxymethyl methylene protons also shifted. This may be due to the doping effect of lanthanides metal ions.

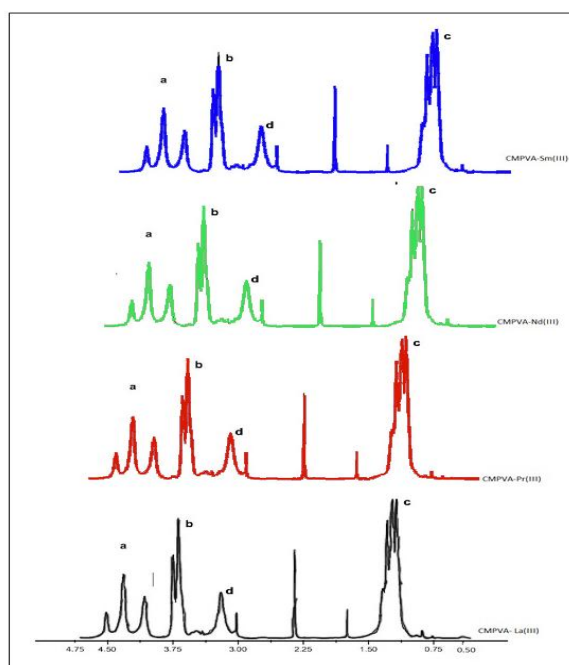


Figure 5. NMR spectra of DOPED CMPVA

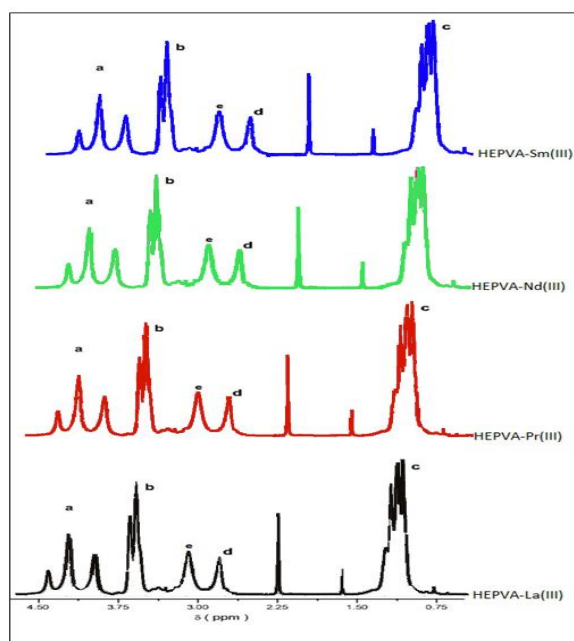


Figure 6. NMR spectra of DOPED HEPVA

The signals at 3.16, 2.48 and 1.89 ppm were attributable to the following solvent contaminants methonal, DMSO and acetic acid respectively as shown in Figure-5 and 6.

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