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Modification of cationic polymer conjugates using advance chemical methods

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Abstract

The synthesis and characterization of modified polyvinyl alcohol conjugates was studied by using modified chemical method. Characterizations of MPVA were carried out by using FTIR, ¹HNMR, XRD. It showed that, 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. 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: Modified 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 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 [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 [5].

2. Material and Methods

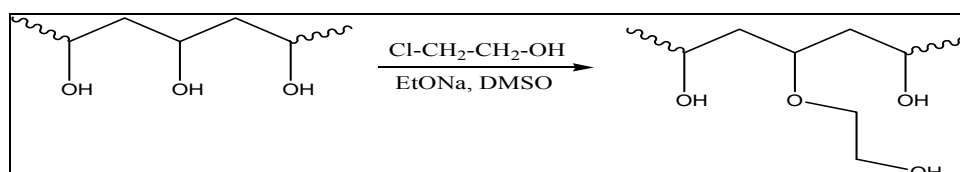
All the chemicals used in this work were obtained from Merck. Following advance methods are used for modification of PVA

❖ Hydroxyethylation of PVA Using Chloroethanol

Chemical Required: Polyvinyl alcohol, Sodium metal, ethanol, anhydrous Dimethyl sulfoxide, chloroethanol, methanol

3. 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 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 vaccum. The resulting sodium polyvinyl alcoholate was dissolved in 200 ml DMSO and 26 ml of freshly distilled chloroethanol was added. The mixture was stirred for 5 hours at 90 °C temperature. The polymer solution was precipitated into methanol to give a florescent white solid (**Scheme-1**).



Scheme-1: Hydroxyethylation of PVA with Chloroethanol

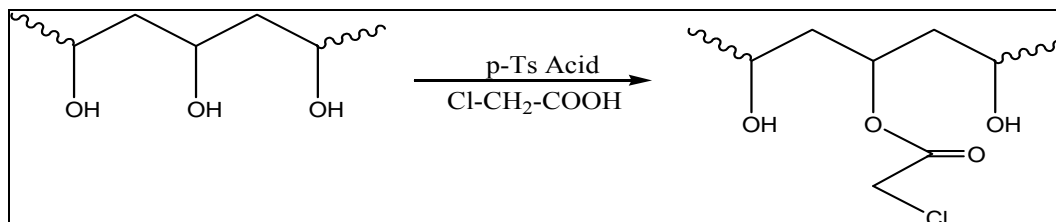
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❖ **Chloroacetylation of PVA with Chloroacetic Acid**

Chemical Required: Polyvinyl alcohol, para-toluenesulphonic acid, ethanol, 1, 2-dichloroethane, chloroacetic acid, sodium carbonate.

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 [2] several times into ethanol (**Scheme -2**).



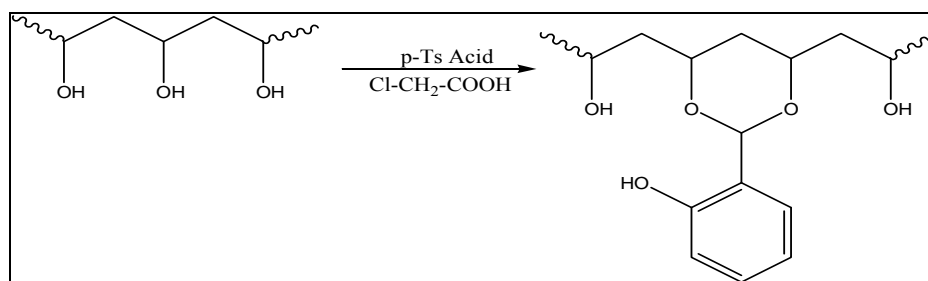
Scheme -2: Chloroacetylation of PVA with Chloroacetic Acid

❖ **Acetalization of PVA with Salicylaldehyde**

Chemicals: Polyvinyl alcohol, salicylaldehyde, 5% aqueous sulfuric acid, Dimethyl sulfoxide 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 [2] by a large amount of methanol (**Scheme -3**).



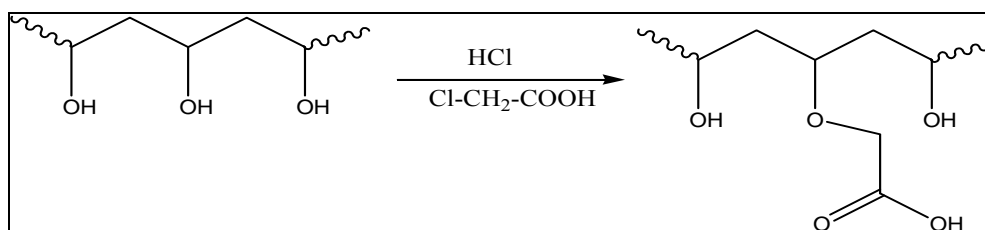
Scheme -3: Acetalization of PVA with Salicylaldehyde

❖ **Carboxymethylation of polyvinyl alcohol with MCAA**

Chemical Required: Polyvinyl alcohol, aqueous potassium hydroxide, monochloro acetic acid, 0.1 N hydrochloric acid and 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 [2] from the solution using methanol. The process was repeated till the polymer became free of chloride ions (**Scheme- 4**).



Scheme-4: Carboxymethylation of polyvinyl alcohol with MCAA

Characterization 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 conjugated under investigation were recorded on Shimadzu FTIR-8101A Spectrophotometer between 400 and 4000 cm⁻¹. XRD patterns of the modified PVA samples were recorded at using Phillips PW-1700, automatic X ray-diffractometer using Cu K α radiation of wavelength 1.544 Å. 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 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 Bruker Avance-II 400 NMR spectrometer on 300 MHz and 75 MHz respectively. The chemical shifts measured are in PPM.

3. Results and discussions

Modified PVA is then characterized by various techniques are as follows,

❖ 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 [7]. 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.	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, 1050.
3.	CMPVA	3240, 2510, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1705.
4.	CAPVA	3340, 2910, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1770.
5.	ACPVA	3340, 2910, 1720, 1655, 1568, 1440, 1330, 1100, 920, 850, 1150.
6.	Literature values	3335, 2910, 1720, 1650, 1555, 1440, 1330, 1090, 900, 855.

The FTIR spectra of pure PVA film, MPVA are presented in figure-1, it showed the absorption peaks of PVA at about 3349 cm^{-1} (-OH, stretch), 2911 cm^{-1} (-CH₂, stretch), 1660 cm^{-1} (C=C), 1568 cm^{-1} (CH₂, b), 1435 cm^{-1} (CH-OH), 918 cm^{-1} (C-C), $851(\text{CH}_2, \text{b}) \text{ cm}^{-1}$ [8, 9]. Characteristic absorption peaks of HEPVA are at 3240 cm^{-1} due to O-H stretching and at 2510 cm^{-1} due to CH stretching. The characteristic absorption of the HEPVA is the band at 1050 cm^{-1} , which is assigned to the stretching vibration of C-O-C Linkage, and other band observed at 1655 cm^{-1} (C=C), 1568 cm^{-1} (CH₂, b), 1440 cm^{-1} (CH-OH), 920 cm^{-1} (C-C), $850(\text{CH}_2, \text{b}) \text{ cm}^{-1}$ [10].

Characteristic absorption peaks of CMPVA are at 3240 cm^{-1} due to O-H stretching and at 2510 cm^{-1} due to CH stretching. The characteristic absorption of the CMPVA is the band at 1705 cm^{-1} and 1690 cm^{-1} , which is assigned to the stretching vibration of C=O linkage, and other band observed at 1655

cm^{-1} (C=C), 1568 cm^{-1} (CH₂, b), 1440 cm^{-1} (CH-OH), 920 cm^{-1} (C-C), $850(\text{CH}_2, \text{b}) \text{ cm}^{-1}$ [11].

Characteristic absorption peaks of CAPVA are at 3190 cm^{-1} due to O-H stretching and at 2390 cm^{-1} due to CH stretching. The characteristic absorption of the CAPVA is the band at 1770 cm^{-1} , which is assigned to the stretching vibration of -O-CO- Linkage, and other band observed at 1655 cm^{-1} (C=C), 1568 cm^{-1} (CH₂, b), 1440 cm^{-1} (CH-OH), 920 cm^{-1} (C-C), $850(\text{CH}_2, \text{b}) \text{ cm}^{-1}$ [12].

Characteristic absorption peaks of ACPVA are at 3180 cm^{-1} due to O-H stretching and at 2400 cm^{-1} due to CH stretching. The characteristic absorption of the ACPVA is the band at 1150 cm^{-1} , which is assigned to the stretching vibration of acetal Linkage, and other band observed at 1655 cm^{-1} (C=C), 1568 cm^{-1} (CH₂, b), 1440 cm^{-1} (CH-OH), 920 cm^{-1} (C-C), $850(\text{CH}_2, \text{b}) \text{ cm}^{-1}$ [13].

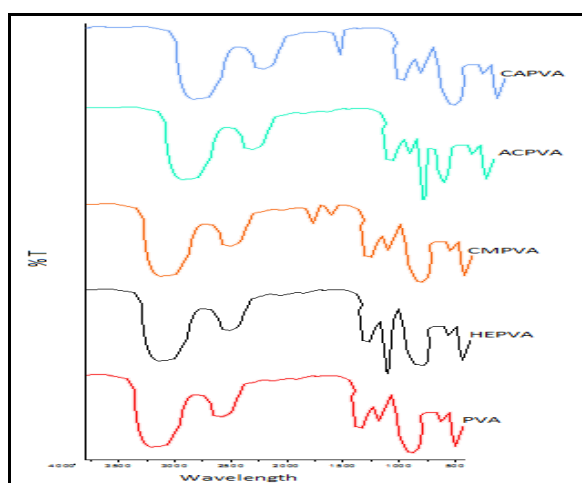


Fig 1: FTIR spectra of MPVA

a. Characterization Modified PVA by using XRD

The XRD profiles of pure PVA, MPVA with lanthanide metal ions are shown in Figure-2. It showed the x-ray diffraction of PVA and MPVA samples at room temperature in the scanning range $6^\circ \leq 2\theta \leq 60^\circ$. Spectrum (a) 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 (101) reflections [14]. The appearance of sharp reflections and

diffuse scattering is characteristic of crystalline and amorphous phases of conventional semi-crystalline polymers [15]. However, spectrum (e) of CMPVA shows a broad amorphous halo with a scattered intensity maximum corresponding to $2\theta = 21^\circ$. 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, they show a liquid-like x-ray pattern [16]. XRD patterns (b) HEPVA and (c)

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 is decreased upon modification. However, XRD pattern (d) 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 [17-21]. 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 (Fig.-2).

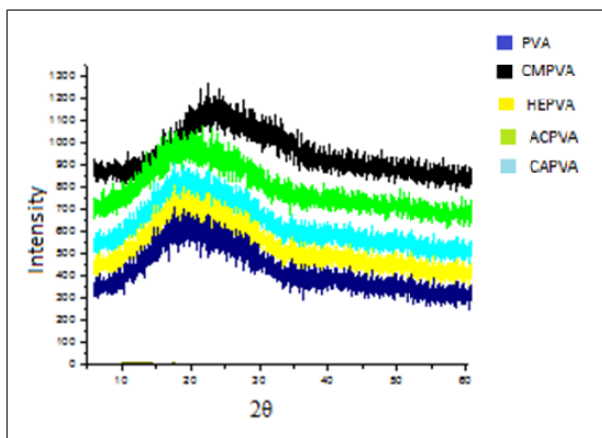


Fig 2: XRD Spectra of pure PVA and MPVA.

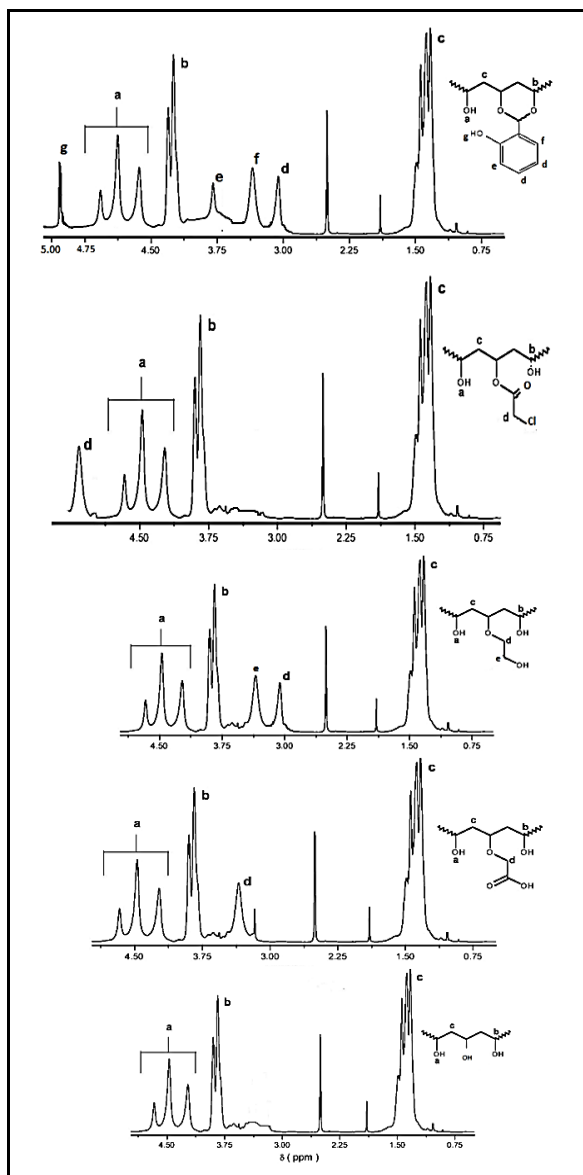


Fig 3: NMR spectra of PVA and MPVA

b. Characterization Modified PVA by using ¹H NMR

¹H NMR gives the information about the type of protons present in the polymer conjugates. The ¹H NMR spectra of pure PVA, MPVA as shown Fig-3 below, CMPVA 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 and c were ascribed to the PVA polymer backbone (methine and methylene protons respectively). The signal at 3.50 ppm was attributed to the carboxymethyl methylene protons.

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 signal at 3.50 and 3.12 ppm was attributed to the chloroethylene methylene protons.

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 was 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 as shown in Figure-3.

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