

Structural and Impedance Enquiry on Biodegradable Blend Polymer Electrolytes of Cornstarch and Polyvinyl Pyrrolidone

M. Anandha Jothi, D. Vanitha, S. Asath Bahadur

Abstract: Biopolymer based Solid polymer blend electrolytes had been prepared utilizing Cornstarch (CS) and Poly vinyl pyrrolidone (PVP) by the technique of solution casting. The readied electrolytes were described by XRD, FTIR and Impedance investigation. The structural properties of CS and PVP blend Polymer Electrolytes (PEs) are dissected by XRD. The interaction among PVP and CS is considered by FTIR investigation. The electrical conductivity is calculated utilizing impedance analyser. The blend of 80wt% CS and 20wt% PVP is having the high conductivity ($4.90217 \times 10^{-9} \text{ S cm}^{-1}$) and low activation energy (0.16 eV). The temperature dependent conductivity obeys the Arrhenius behaviour.

Keywords: Cornstarch, PVP, XRD, FTIR and Conductivity studies

I. INTRODUCTION

Solid polymer electrolytes (SPE) have impending application in electrochemical devices. It has simple fabrication, good electrode-electrolyte interface and biggest problem in electrochemical devices, such that leakage doesn't occur in SPE based system. Control of plastic waste is a worldwide problem in recent years. To overcome this issue, renewable and biodegradable material-based research is enormously increased. Bio polymers are best alternate for these types of synthetic polymers. Starch is a standout amongst the most prevalent renewable and biodegradable polymers to partially or completely supplant plastic polymer. Biopolymer starch is made out of glucose units and having two principle constituents are, amylase and amylopectin. Long chain of α -D glucose units connected together by α -1,4 glycoside linkages are nearness in amylose and α -1,6 linkages are interlinked with α -1,4 linkages of glucose units in amylopectin [1]. The overall measures of amylose and amylopectin rely on the plant source. Behind this, the selected biopolymer, cornstarch (CS) is having tiny particle size that offers enhanced dispersions in blends. CS is non-toxic, available in abundance, biodegradable and

water soluble. 30% amylase and 70% amylopectin are present in CS granules [2]. The advancements of starch-based items are constrained by poor mechanical quality, high sensitivity to moisture, brittle, quickly degrades when exposed to water and its productive barrier against low polarity compound. In endeavors to beat this drawback, there have been numerous endeavors to join starch with synthetic polymers. By using artificial polymers which are biodegradable, starch-based polymer blends are prepared to use in the biomedical and natural fields. Biocompatible, biodegradable, nontoxic, extraordinary natural quality, effectively dissolvable in water and other polar solvents and amazing film-framing limit [3] as per these properties, Poly vinyl pyrrolidone (PVP) has gotten uncommon consideration than other conjugated polymers to blend with CS. Misleadingly PVP has been observed to be inert and it shows a sturdy affinity for a complex arrangement with a extensive collection of littler atoms [4]. Subject to electrical and optical properties of PVP is utilized for electrochemical devices, for example, energy storage devices with high limit. The present work principally examines the structure and ionic conductivity of CS-PVP mix biodegradable SPE. In this way it got incredible consideration and was widely researched.

II. EXPERIMENTAL

A. Materials and Preparation method

CS with a linear formula of $\text{C}_6\text{H}_{10}\text{O}_5$ was purchased from SRL chemicals, Poly(vinyl pyrrolidone) with a linear formula of $\text{C}_6\text{H}_9\text{NO}$ was obtained from (S D Fine Chem Ltd., India). The biodegradable polymer blend electrolytes were prepared in different weight ratios of CS:PVP (100:0), (90:10), (80:20), (70:30), (60:40) and (50:50) by solution casting technique using DD water as solvent. The solution of CS was prepared in 50 ml of 1% acetic acid and heated upto 75°C for 20 minutes. Various wt % of PVP were added to the solution after the solution attains the room temperature. Then the solutions were mixed and stirred for 24 hours until became homogenous and then transferred to Polypropylene Petri dishes. The solvent was permitted to evaporate gradually at room temperature. The prepared CS and PVP blend electrolytes were excluded from Petri dish for further analysis. All samples were stored airtight under room temperature. Table I shows the coding of different composition of the prepared polymer electrolytes.

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Table -I: Sample code assignment of different composition ratio of CS:PVP

Composition Ratio (CS:PVP)	Sample code
100:0	VP-00
90:10	VP-10
80:20	VP-20
70:30	VP-30
60:40	VP-40
50:50	VP-50

III. RESULTS AND DISCUSSION

A. XRD Analysis

The preference of a proper extent of the polymer blend is its capability to act as a polymer host in electrolytes. The selection manages the crystallinity of the polymer blend. Two broad crystalline humps show up at $2\theta = 17^\circ, 19.8^\circ, 21.9^\circ,$ and 30.4° [5,6] for the XRD of pure CS film (100 wt% starch). To diminish the crystallinity of CS, different wt% of PVP is included. From the XRD, it is obviously detectable that the perceptible humps in the XRD become indistinct with increasing the PVP content. In the XRD pattern of the sample VP-20 is not having any distinct peak indicating the amorphous nature of the blend [7]. The advancement of a profoundly amorphous nature in this sample might be perceived as a key factor that acquires an enrichment of ions.

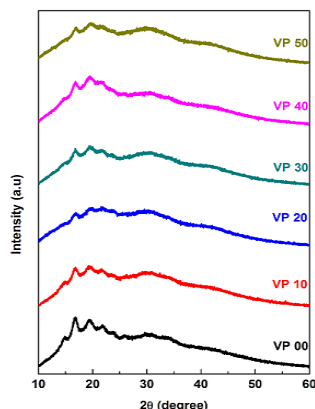


Fig. 1. X-ray diffractograms for different compositions of CS and PVP

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B. FTIR Analysis

FTIR is competent tool to study the local structural changes

in polymer. The infrared spectra of these materials differ according to their composition and assist in confirming the complex formation among polymer matrices. From FTIR spectra, the observed bands at 3285 and 2927cm^{-1} are pertaining to the intermolecular hydrogen-bonded O–H stretching and aliphatic stretchable C–H mode of pure CS correspondingly. The band appeared at $1149\text{cm}^{-1}, 995\text{cm}^{-1}$ and 863cm^{-1} which belongs to C–O stretching, C–O in C–O–C groups and C–H ring mode are mainly due to the starch and also used to monitor the starch content in the polymer blend. Some FTIR band assignment is exposed in Table II. The intensity of the above said bands decreases by lowering the concentration of CS. The peak observed at 1006cm^{-1} in the FTIR could be connected with C–O–H vibration [8]. It could be decreased by addition of PVP. The peak at $1,292\text{cm}^{-1}$ is typical for C–N bond in PVP was newly presented except VP-00 sample. The band at 1437cm^{-1} is allocated to the stretchable C–N vibrations and the addition of CH_2 groups in the pyrrole ring of PVP [9, 10]. Jie-Jun Zhu et al reported the infrared transmission spectrum for pure PVP illustrates that the peak of the C=O at 1660cm^{-1} [11, 12] was increased and vaguely moved to approximately 1647cm^{-1} after blended with CS.

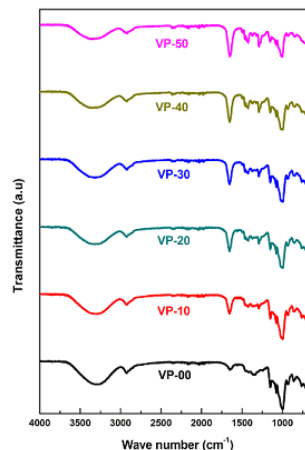


Fig. 2. FTIR for different compositions of CS and PVP

Table- II: FTIR assignment

Wave number (cm^{-1})	Assignments
1651	C=O stretching of PVP
1437	C–N stretching
1281	C–H deformation
1149	C–O stretching
995	C-O in C-O-C groups
863	C-H ring

C. Impedance analysis

Impedance spectroscopy gives a better perceptible in the conduction method and mobility processes. To calculate the ionic conductivity of electrolyte solutions, the following relationship is used:

$$\sigma = l / R_b A \text{ (S cm}^{-1}\text{)} \quad (1)$$

Where σ is the conductivity of the sample in S cm^{-1} , the thickness of the polymer film is l in cm, the bulk resistance of the polymer film is R_b in Ω and the area of the electrode/electrolyte is A in cm^2 .

From fig. 3a, a semi-circle alone is observed for various composition of CS and PVP such as VP-00, VP-10, VP-20, VP-30, VP-40 and VP-50 blend polymer electrolytes. This semicircle is formed by the parallel combination of immobile charge (CPE – constant phase element) and mobile charge carrier (resistor) in polymer chain. The electrical comparable circuit symbol is usually utilized in impedance investigation since it is quick, straightforward and gives the entire representation of the framework [13]. R_b value is measured from the intercept of the semicircle with the X-axis at low frequency region. The conductivity has been increased up to VP-20 due to increase the amorphous nature (raise the wt% of PVP) in PEs at ambient temperature. Above VP-20 conductivity has been decreased due to decrease the amorphous nature in PEs and increase in conductivity by Ion migration and exchange through this complexation sites. The conductivity of the different concentration of CS and PVP blend PEs at low and at high temperatures are listed in table III. The higher conductivity obtained for VP-20 is $4.90217 \times 10^{-9} \text{ S cm}^{-1}$ in the room temperature.

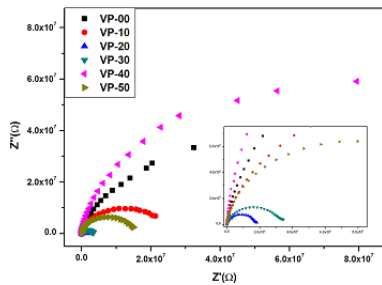


Fig. 3a. Nyquist plot for various compositions of CS and PVP

The fig. 3b shows the conductivity of the prepared films at various temperatures. From this, it is observed that the conductivity of the polymer electrolyte rises with temperature and spike is present due to the electrode and electrolyte interface effect. The conductivity of VP-20 polymer electrolyte increased to reach the value $1.15675 \times 10^{-8} \text{ S cm}^{-1}$ at 358K.

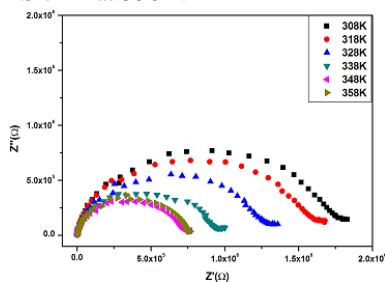


Fig. 3b. Nyquist plot for VP-20 at various temperatures

Table- III: Conductivity for all compositions of CS:PVP at low & high temperature and Activation energy

Sample	$\sigma \text{ (S cm}^{-1}\text{)}$		$E_a \text{ (eV)}$
	308K	358K	
VP-00	1.75999×10^{-10}	8.16905×10^{-10}	0.2
VP-10	3.53291×10^{-10}	1.50407×10^{-9}	8
VP-20	4.90217×10^{-9}	1.15675×10^{-8}	0.1
VP-30	3.1392×10^{-9}	8.40801×10^{-9}	6
			9

VP-40	1.09657×10^{-10}	3.04997×10^{-10}	0.3
VP-50	8.08774×10^{-10}	4.26909×10^{-9}	0
			0.2
			7

D. Conductance spectra analysis

In frequency dependence conductance spectra is helpful for know about the ion dynamics and conductance behavior in the SPEs at lower frequency to higher frequency and it is shown in fig. 4a. From frequency dependent conductance spectra, two regions are observed. There are lower frequency dispersion region and higher frequency dispersion region.

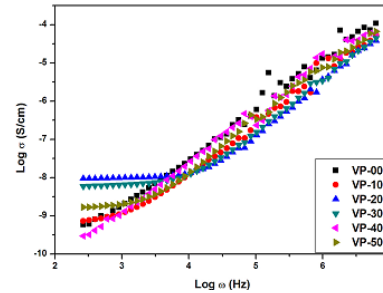


Fig. 4a. Conductance spectra for different concentrations of CS/PVP

At lower frequency dispersion region, the polarization effect shows the way to reduce the number of free ions and ultimately drop in conductivity at electrode interface with electrolyte and also space charge polarization. The higher conductivity in the high frequency region is due to the more prominent portability of charge carriers and quicker ion hopping. Along these lines, the ion exchange process happens all the more viably at higher frequencies. The extrapolations of low frequency plateau region to meet along y-axis is used for determine the dc conductivity.

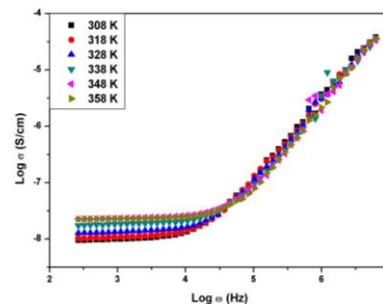


Fig. 4b. Conductance spectra for VP-20 at different temperature

From fig. 4a, VP-20 sample reaches high dc conductivity than other samples. At lower frequencies, the conductance spectra have variation due to the space charge polarization but there is no variations are observed in the higher frequency region. From 308K to 358K, conductivity variations in high conducting sample observed particularly at low frequency as clearly shown in fig. 4b.

E. Temperature dependent conductivity

The temperature dependent conductivities of CS and PVP polymer blend electrolyte system investigated at temperature range of 313 K to 353 K as shown in fig. 5. When the temperature increases the polymer matrices have been expanded to form the free volume, then ions are easily migrated through the unoccupied spaces of the polymer matrices. In this way conductivity of ions in polymer electrolytes have

been enhanced with increasing temperatures according to ion hopping mechanism [14].

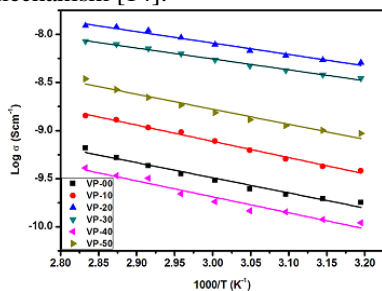


Fig. 5. Arrhenius plot for samples VP-00, VP-10, VP-20, VP-30, VP-40 and VP-50

Fig. 5 Draws between log σ and $1000/T$ graph. The conductivities are linearly increased by rising temperature in all the polymer electrolyte samples. All prepared samples to obey the Arrhenius behavior. Using linear fit, to find the slope of the straight line. The activation energy of the polymer electrolytes has been calculated with help of this slope value, using the following formula,

$$\sigma(T) = \sigma_0 \exp(-E_a / KT) \quad (2)$$

Table III gives the observed conductivity and the activation energy values. The activation energy is found to be low (0.16eV) for the high conductivity sample VP-20 (80 wt. % of CS + 20 wt. % of PVP).

IV. CONCLUSION

Different compositions of CS and PVP blend polymer films have been prepared by solution cast technique. From the XRD results, 80 wt. % of CS + 20 wt. % of PVP was observed to be the most reasonable proportion because of the expansion in amorphous nature. The FTIR analysis reveals that the interchain hydrogen bonding between hydroxyl groups of CS and carbonyl groups of PVP. The higher conductivity at ambient temperature is found to be $4.90217 \times 10^{-9} \text{ Scm}^{-1}$ for the composition of VP-20. All the prepared electrolytes obeyed the Arrhenius rule. High conducting sample VP-20 has low activation energy of 0.16eV.

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