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Effect of NH_4NO_3 on Conductivity of biopolymer electrolyte based on Potato starch

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Abstract
Various compositions of Potato starch and NH_4NO_3 based biopolymer electrolytes have been prepared by using Solution Casting Technique. The Prepared biopolymer electrolytes are characterized by using XRD, FTIR, AC Impedance analysis etc… XRD analysis confirms the amorphous nature of the biopolymer electrolytes. The FTIR analysis reveals the complex formation between the biopolymer (Potato starch) and Salt (NH_4NO_3). The maximum conductivity is found to be 5.67×10^{-5} S/cm at ambient temperature for 30 Potato starch: 70 NH_4NO_3 biopolymer electrolyte among the prepared biopolymer electrolytes.

Keywords: XRD, FTIR, AC Impedance analysis

1. Introduction
In recent years, biopolymer electrolytes attract the attention of many researchers because of its chemical structure differences, rich variety, low cost and biodegradable nature etc. Biopolymers are suitable substitute for synthetic polymers because most of the synthetic polymers are insoluble in solvents and non-biodegradable material [1]. Many biopolymers such as (Starch, Corn starch, Potato starch, Pectin, Amylose and Polysaccharide) are easily available in nature. But the biopolymer Potato starch has a great attention due to its rich variety and abundances in nature. Many people have already worked with biopolymer Potato starch because of its good film forming nature and high ionic conductivity [2]. A literature study reveals that the ammonium salts are good proton donors [3]. The author Hemalatha *et al.* has already reported the ionic conductivity of NH_4SCN doped with Potato starch biopolymer electrolytes as ~ 3.67×10^{-4} S/cm [4]. The author Manindra Kumar *et al.* has already reported on the conductivity studies of NH_4I doped with Potato starch based biopolymer electrolytes and ionic conductivity value in the order of ~ 10^{-4} S/cm [2]. In the present work, different molar mass percentage of salt (NH_4NO_3) has been added with biopolymer Potato starch. These Polymer electrolytes are subjected to different studies such as XRD, FTIR and AC impedance.

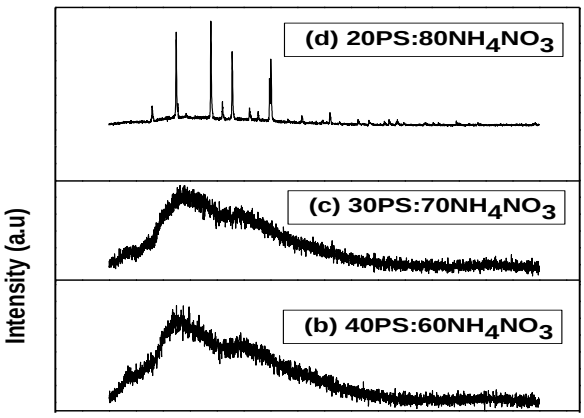
2. Experimental Procedure
2.1 Sample Preparation
In the present study, Potato starch with molecular weight= 162.14 g/mol (LOBA CHEMIE) and NH_4NO_3 with molecular weight 80.043 g/mol (REACHEM) are used as starting material with Water as solvent. Different molar ratios of Potato starch: NH_4SCN as (100:0), (40:60), (30:70) and (20:80) have been prepared by Solution Casting Technique. In this technique, appropriate weight of Potato starch and NH_4NO_3 have been dissolved individually in Water and these solutions have been mixed together and stirred well by using magnetic stirrer to obtain a homogeneous mixture. The obtained mixture is casted in Propylene petridish and is subjected to vaccum dried at 40°C for 1 day. Mechanically strong, transparent and flexible films have been obtained.

2.2 Characterization
1. Structural study
X-ray diffraction patterns of the prepared samples have been recorded at room temperature on a Philips X' Pert PRO diffractometer using CuK_α radiation in the range of $2\theta = 10°$ to 90°.

2. Vibrational study
FTIR spectra have been recorded for the polymer electrolyte films using a SHIMADZU- IR Affinity-1 Spectrometer in the range of $400cm^{-1}$ to $4000cm^{-1}$ at room temperature.

3. AC impedance study
Conductivity measurements have been carried out by using a HIOKI – 3532 LCZ meter in the frequency range of 42 Hz – 1MHz over the temperature range of 303K – 343K.

3. Results and Discussion
3.1 XRD analysis
X-ray diffraction (XRD) studies have been carried out to inquire the occurrence of the amorphous nature of the bio polymer electrolytes. Figure 1 depicts the XRD pattern of pure Potato starch and Potato starch doped with NH_4NO_3 in different molar ratios. A broad diffraction peak around 20° in the Fig 1 (a) is the characteristic peak of pure Potato starch.



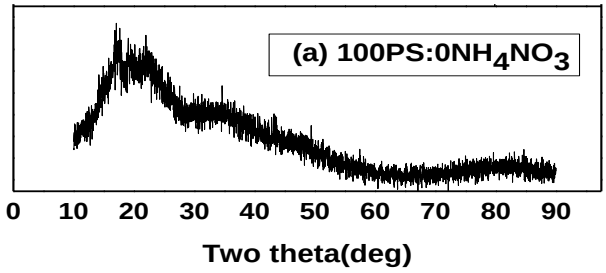


Fig 1: XRD Spectra of all biopolymer electrolytes

The addition of salt NH_4NO_3 enhances the amorphous nature of the polymer Potato starch. This result can be interpreted in terms of the Hodge et al. criterion which establishes a correlation between the intensity of the peak and the degree of crystallinity [5].

Table 1: Position of the diffraction peak, Full width half maximum & Conductivity of all electrolytes

Composition (mol %)	Position (2θ°)	FWHM (2θ°)	Conductivity (S/cm)
Pure Potato starch (100PS:0NH_4NO_3)	20.37	11.64	5.07×10^{-10}
40PS:60NH_4NO_3	28.24	23.26	5.23×10^{-5}
30PS:70NH_4NO_3	29.03	23.86	5.67×10^{-5}
20PS:80NH_4NO_3	22.37	---	1.67×10^{-6}

From the Table 1 it has been observed that the broadness of this peak increases and its relative intensity slightly decreases with increase of NH_4NO_3concentration up to 70 mol%. The peaks at 2θ=22.37°, 29.05°, 39.9° [JCPDS. 83- 0520] corresponding to characteristic peak of Pure NH_4NO_3 are present in the 80 mol% NH_4NO_3 doped biopolymer electrolyte (Figure 1d). It indicates the presence of some undissociated salt in the polymer electrolyte leading to lower ionic conductivity [6].

3.2 Fourier Transform Infrared analysis

The purpose of measurement of Fourier transform infrared spectroscopy (FTIR) of pure Potato starch and Potato starch-(NH_4NO_3) polymer electrolytes are to confirm the complex formation of the ammonium salt with polymer. Figure 2 represents the FTIR spectra of various compositions of Potato starch doped with NH_4NO_3. The vibrational frequencies observed in the FTIR spectra of Potato starch – NH_4NO_3 polymer electrolytes are given in Table 2

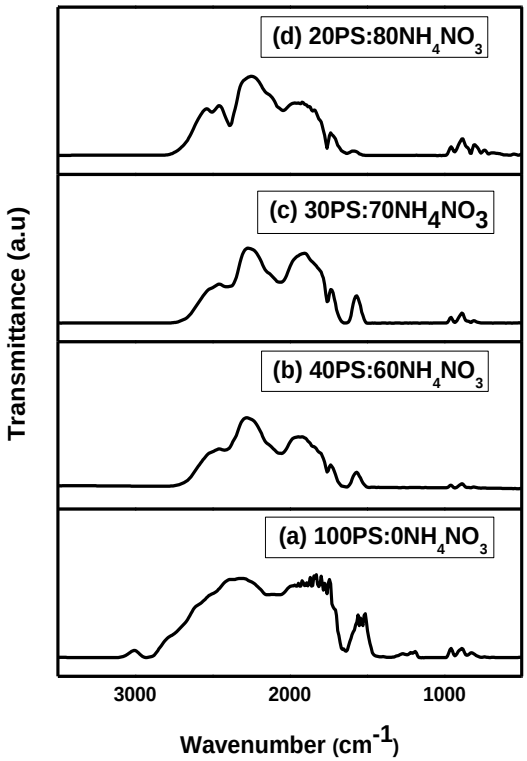


Fig 2: FTIR Spectra of all biopolymer electrolytes

Table 2: Vibrational bands for all biopolymer electrolytes

Vibrational peaks of the biopolymer electrolytes (cm^{-1})				Assignment
Pure Potato starch	40 PS:60 NH_4NO_3	30 PS:70 NH_4NO_3	20 PS:80 NH_4NO_3	
933	933	933	933	O-H (b)
1759	1759	1759	1759	C=O (s)
2931	2939	2954	2924	C-H (s)

The characteristic peak of pure Potato starch at 2931 cm^{-1} assigned to C-H stretching is shifted to 2939 cm^{-1}, 2954 cm^{-1}, 2924 cm^{-1} in 40:60, 30:70, 20:80 compositions of Potato starch: NH_4NO_3 polymer electrolyte respectively [1]. The peaks at 933 cm^{-1} and 1759 cm^{-1} attributed to O-H bending and C = O stretching vibrations of pure Potato starch has got no change in the frequencies of the complex. FTIR confirms the complex formation between the salt and Polymer.

3.3 AC Impedance analysis

Electrical properties of materials are characterized by AC impedance technique. Figure 3 shows the complex impedance plots of Potato starch – NH_4NO_3 polymer electrolyte for different concentrations at 303K. The impedance can be calculated from the semicircle or the intercept of spike on the z′ axis. The ionic conductivities are calculated using the relation,

$\sigma = l/R_b A$

where l is the thickness, R_b is bulk resistance and A is the known area of the electrolyte film.

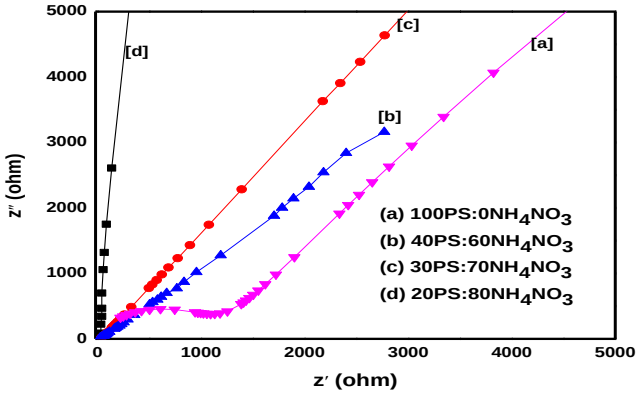


Fig 3: Cole-Cole plot of all biopolymer electrolytes

From figure 3a the plot of pure PS consists of a high frequency semicircle represented by a frequency- dependent bulk capacitor C_b parallel to bulk resistor R_b. From figure 3b- 3d the plots consists of a low frequency spike due to the blocking electrode. From the figure 3c, it is found that 30 Potato starch: 70 NH_4NO_3 has the highest conductivity 5.67×10^{-5} S/cm at ambient temperature (303K). The semicircle disappears in the salt NH_4NO_3 added samples as shown in the (fig 3b- 3d). The decrease in conductivity at higher concentration of 20 PS and 80 NH_4NO_3 may be due to the formation of ion aggregates [7].

4. Conclusion

Potato starch-based polymer electrolytes with different concentrations of ammonium nitrate have been prepared using the solution casting technique.

- The XRD pattern reveals the increase in amorphous nature of the Potato starch with the addition of NH_4NO_3.
- FTIR studies reveal the complex formation between the salt NH_4NO_3 and polymer matrix Potato starch.
- The highest ionic conductivity has been found to be $5.67\times10^{-5}Scm^{-1}$ for 30Potato starch: 70 NH_4NO_3 polymer electrolyte from the Cole- Cole Spectra.

5. Acknowledgement

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6. References

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