Vibrational and Dielectric Studies of Plasticized Biopolymer Electrolytes Based On Potato Starch:NH₄Cl

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Abstract— Bio polymer electrolytes based on Potato starch as host polymer, Ammonium chloride (NH₄Cl) as salt and propylene carbonate (PC) as plasticizer have been prepared by Solution Casting Technique using distilled water as a solvent. The prepared polymer electrolytes are subjected to Vibrational and Dielectric studies. The FTIR analysis reveals Complex formation among the polymer, salt and plasticizer of the electrolytes. The dielectric behavior of the electrolyte has been discussed. The dielectric spectra exhibit the low frequency dispersion due to space charge accumulation at the electrode-electrolyte interface.

Keywords—Biopolymer, Potato Starch, PC, FTIR, Dielectric.

I. INTRODUCTION

The polymer electrolytes having higher ionic conductivity play a major role in the ionic devices namely electrochromic devices, sensor and super capacitors^[1]. Different starches like arrowroot, corn and potato starches are utilized for research work [2]. These Starches are abundance in nature [3]. Literature studies reveal that Plasticizers such as Propylene carbonate, Ethylene carbonate could enhance the ionic conductivity of polymer electrolytes. PC is an organic, colourless and odorless organic compound. It is also well known as highly polar and aportic solvent [4]. Potato starch has been chosen as host polymer for the present work because the potato starch results in soft flexible film with high conductivity in comparison to others^[5]. Now an attempt has been made to enhance the ionic conductivity of 40 PS and 60 NH₄Cl by incorporating the plasticizer propylene carbonate in different molar ratios. The prepared polymer electrolytes have been subjected to different analysis.

II. EXPERIMENTAL PROCEDURE

Sample Preparation

Bio Polymer of Potato starch with molecular weight= 162.14 g/mol (LOBA CHEMIE), NH₄Cl with molecular weight= 53.49 g/mol (REACHEM) and PC with molecular weight= 102.09 g/mol (AR grade Mecury) are used in the Present work. Water solutions of Potato starch and NH₄Cl are stirred continuously with a magnetic stirrer. After complete dissolution of the salt, PC is added accordingly and the mixtures are stirred well for several hours to obtain homogeneous solutions. The obtained mixture is casted in Propylene pertridish and is subjected to vaccum dried at 40°C for 1 day. Mechanically storng, transparent and flexible films have been obtained.

Characterization

1). 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.

2) 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.

III. RESULTS AND DISCUSSION

Fourier Transform Infrared analysis

FTIR Spectroscopy is a versatile tool to analyze the polymeric materials since it provides information about the interaction between the polymer, salt and plasticizer of the electrolytes. The FTIR spectrum of optimized systems of 40 PS: 60 NH₄Cl and 40 PS: 60 NH₄Cl: X PC (X=20, 60 mol %) Polymer electrolytes. are shown in Figure 1.

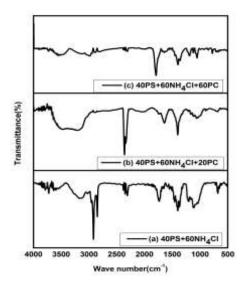


Figure.1. FTIR spectra of all Biopolymer electrolytes

The positions of vibrational bands observed in the FTIR spectra of 40PS:60 NH₄Cl :X PC (X=0,20,60) and their assignments are listed in Table 1.The vibrational peaks at 3595cm⁻¹ are attributed to stretching vibrations of O-H present in the pure potato starch^[6]. The peak appears at 1037 cm⁻¹ is attributed to C-O bond stretching of the C-O-C group in starch^[7]. The peaks at 1202 cm⁻¹ and 2918 cm⁻¹ are attributed to N-H stretching vibrations of NH⁺ present in the salt NH₄Cl ^[2]. The peaks at 786 cm⁻¹ are attributed to Ring deformation of PC. The characteristic peaks at 1111 cm⁻¹,1164 cm⁻¹ are attributed to stretching vibrations of C-O present in the plasticizers of propylene carbonate. The vibrational peaks at 1400 cm⁻¹,1455 cm⁻¹ are attributed to CH₂ bending deformation mode of CH₃ group of PC^[8]. The peaks at 1371 cm⁻¹ and 1731 cm⁻¹ are attributed to C-H symmetric deformation, C=O symmetric stretching mode of PC [9]. The shift in the peak positions and changes in the intensity of the bands in the FTIR spectra of the samples with and without plasticizers confirm the complex formation between the polymer, the salt and plasticizers.

Vibrational peaks of the biopolymer electrolytes 40PS:60NH ₄ Cl:XPC (cm ⁻¹)			Assignments
786	777	777	Ring deformation of PC
1037	1058	1053	C-O(s) of Potato starch
1111	1115	1120	C-O(s) of PC
1164	1163	1189	C-O(s) of PC
1202	1204	1227	N-H(s) of NH+ of NH4Cl
1371	1318	1358	C-H(sym) of PC
1400	1401	1395	CH ₂ (b) of PC
1455	1453	1452	CH ₂ (b) of PC
1731	1745	1791	C = O (sym) of PC
2918	2945	2988	N-H(s) of NH+ of NH4Cl
3595	3500	3543	O-H(s) of Potato starch

Table 1 FTIR spectral assignments of all Biopolymer electrolytes.

Dielectric Spectra Analysis

The dielectric behavior of any polymeric system may be reported by the real and imaginary parts of the complex permittivity, ε^* which is defined by the relation:

$$\varepsilon *= \varepsilon'(\omega) - \iota \varepsilon''(\omega) \tag{1}$$

Where $\varepsilon'(\omega)$ real a imaginary $\varepsilon''(\omega)$ components are the storage and the loss of energy in each cycle of the applied electric field.

Figure 2. (a, b) represents the frequency dependence of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ for 40PS:60 NH₄Cl:X PC and 40PS:60 NH₄Cl:XPC (X=0,20,60 mol%); polymer electrolytes at 303 K, respectively. The values of dielectric constant (ε') and dielectric loss (ϵ ") are very high at low frequencies and relatively constant at higher frequencies. Such high value of dielectric constant (ϵ ') may be due to the interfacial effects within the bulk of the sample and electrode effects [1]. Figure .3.(a,b) represents the frequency dependence of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ for 40PS:60 NH₄Cl:20PCpolymer electrolytes at different temperature, respectively. At higher frequencies, the periodic reversal of the applied electric field is so high that the dipoles are unable to follow the applied electric

field as a result that there is no excess ion diffusion in the field direction resulting in the decrease in dielectric constant^[10]. High values of ϵ' and ϵ'' at low frequencies have been obtained for the plasticized electrolytes than the unplasticized one. It may be due to the enhanced charge carrier density in the space charge region ^[1].

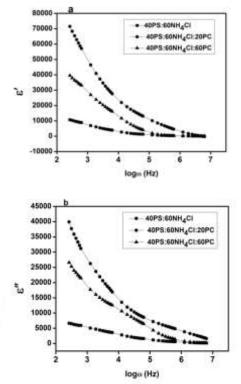


Figure.2. (a & b) Dielectric constant and Dielectric loss spectra of all bio Polymer electrolytes at 303 K

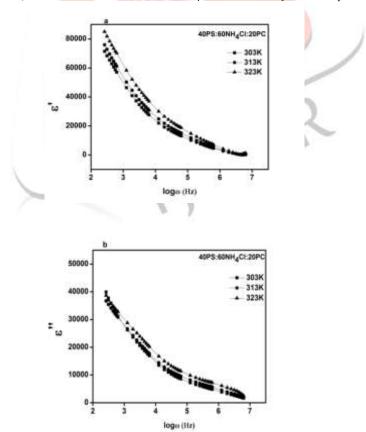


Figure.3. (a & b) Dielectric constant and Dielectric loss spectra of 40PS:60NH₄Cl:20PC bio polymer electrolyte at different temperatures.

IV. CONCLUSION

40PS:60 NH₄Cl and 40PS:60 NH₄Cl: X PC (X=0,20,60 mol%) proton conducting Bio polymer electrolyte have been prepared by solution casting technique. The complex behavior among the polymer, the salt and plasticizers has been confirmed by FTIR studies. High values of Dielectric constant may be due to the enhanced charge carrier density in the space charge region.

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