

Thermal and Structural Studies of Plasticized Biopolymer Electrolytes Based On Potato Starch: NH₄Cl

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Abstract: The 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 plasticized biopolymer electrolytes are subjected to Structural, Thermal and conductivity Studies. The X-ray diffraction analysis confirms amorphous nature of the plasticized biopolymer electrolytes. The Differential Scanning Calorimetry has been employed to find out the glass transition temperature (T_g) of the prepared electrolytes. It has been observed that the ionic conductivity of the biopolymer electrolytes increases with increase in propylene carbonate concentration. The plasticized polymer electrolyte 40 PS: 60 NH₄Cl: 20PC has the ionic conductivity 9.27 X 10⁻⁴ Scm⁻¹ at ambient temperature.

Keywords: Biopolymer, Potato Starch, PC, XRD, DSC.

I. INTRODUCTION

Starch like cornstarch, arrowroot and potato starch etc., attracts scientists due to its rich variety and abundance in nature^[1]. Literature studies reveal that the incorporation of the Plasticizers such as Propylene Carbonate, Ethylene Carbonate etc., to the polymer electrolytes could enhance the ionic conductivity of polymer electrolytes. PC is an organic, colourless and odorless organic compound which is also well known as highly polar and aprotic solvent and has high dielectric constant.

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^[2].

Now an attempt has been made to enhance the ionic conductivity of 40 PS: 60 NH₄Cl biopolymer electrolyte by incorporating the plasticizer propylene carbonate in different molar ratios. The prepared biopolymer electrolytes have been subjected to structural thermal and conductivity studies..

II. EXPERIMENTAL PROCEDURE

A. 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 Merck) 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 Petridis and is subjected to vacuum dried at 40⁰C for 1 day. Mechanically strong, transparent and flexible films have been obtained.

B. Characterization

1) *Structural Analysis:* X-ray diffraction patterns of the products are recorded at room temperature on Philips X'PERT – PRO diffractometer using Cu K α radiation in the range of $2\theta = 10^0$ -80⁰

2) *Electrical Analysis:* 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

A. X-ray diffraction analysis

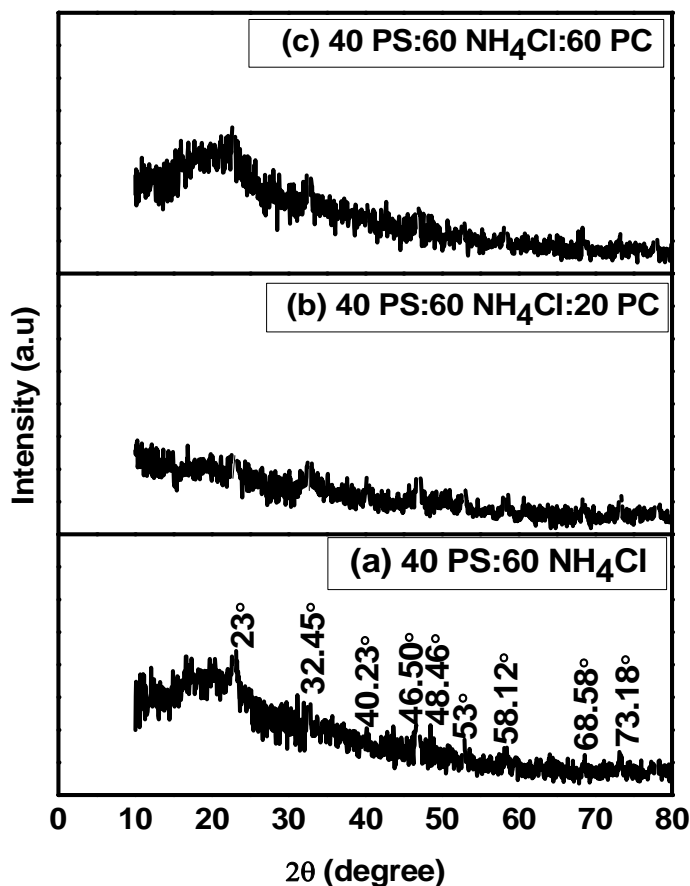


Fig. 1 XRD pattern of all Biopolymer electrolytes

The X-ray diffraction is used to study whether a material is amorphous or crystalline and to determine the crystallite size of the plasticized biopolymer electrolytes. The XRD Patterns of optimized systems of (40 PS: 60 NH₄Cl: X PC) (X=0,20, 60 mol %) polymer electrolytes are shown in Figure.1. The character (Fig.1a)^[3]. This peak disappears in the 40 PS: 60 NH₄Cl: 20 PC (Fig.1b). But it has been found to be slightly shifted to 2θ= 22.49° in the plasticized polymer electrolyte 40 PS: 60 NH₄Cl: 60 PC (Fig.1c). The crystallites size (D) for all bio polymer electrolytes are calculated by using Debye Scherer's equation

$$D = K\lambda / \beta \cos\theta \text{ ----- (1)}$$

Where

λ- the wavelength of the X-ray radiation (1.540 Å)

K- a constant taken as 0.89

θ -the diffraction angle (in degrees)

β -the full width at half maximum (FWHM)

From the table. 1, it is observed that 40 PS: 60 NH₄Cl:20 PC biopolymer electrolyte has got small crystallite size and less relative intensity. The increase in full width half maximum of the characteristic peak reveals the amorphous nature of the polymer electrolyte. This result can be interpreted by Hodge et al. criterion which establishes a correlation between the intensity of the peak and the degree of crystallinity^[4]. The peaks at 2θ = 45°, 40.23°, 46.50°, 48.46°, 53°, 58.12°,68.58° & 73.18° in Fig.1.a are corresponding to crystalline peak of ammonium chloride (NH₄Cl) which has been confirmed by [JCPDS:89-2787,34-06445,34-0710]. It indicates the incomplete dissociation of the salt (NH₄Cl) in the bio polymer electrolyte leading to low ionic conductivity.

These peaks disappear in the plasticized biopolymer electrolytes (Fig.1.b&c). Thus the XRD analysis reveals the complex formation in the polymer matrices.

TABLE I
DIFFRACTION PEAK, CRYSTALLITE SIZE, GLASS TRANSITION TEMPERATURE AND IONIC CONDUCTIVITY OF ALL BIO POLYMER ELECTROLYTES

Composition 40 PS: 60 NH ₄ Cl: X PC (mol %)	Crystallite size (nm)	Glass transition temperature T _g (°C)	Ionic Conductivity (Scm ⁻¹)
X=0	0.952	67.43	8.41 x 10 ⁻⁵
X=20	0.339	54.29	9.27 x 10 ⁻⁴
X=60	0.512	57.96	1.04 x 10 ⁻⁴

B. Differential Scanning Calorimetric Analysis

The differential scanning calorimetry has been employed to find out the glass transition temperature (T_g) of the biopolymer electrolytes. The DSC thermograms of 40PS: 60 NH₄Cl: X PC (X= 0,20, 60 mol %) Plasticized bio polymer electrolytes have been shown in Figure.2.(a, b & c). The addition of plasticizer to 40PS: 60NH₄Cl Bio polymer electrolyte decreases the glass transition temperature (T_g) of unplasticized biopolymer electrolyte from 67.43°C to 54.29°C. The reason may be that the plasticizer propylene carbonate reduces the segmental mobility of the chains of potato starch [5]. The 40 PS: 60 NH₄Cl:20 PC has the lowest glass transition temperature (T_g) leading the highest ionic conductivity. It is concord with impedance analysis.

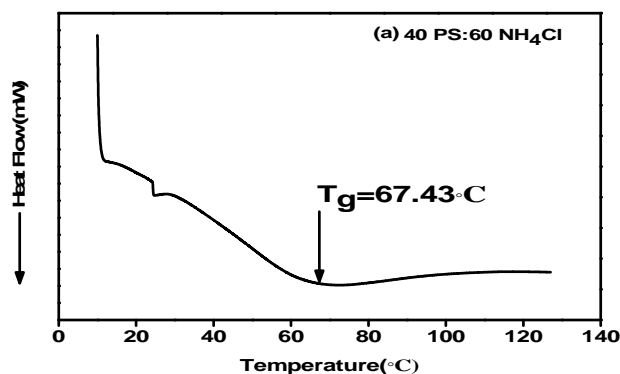


Fig. 2.(a) DSC thermogram of unplasticized biopolymer electrolyte

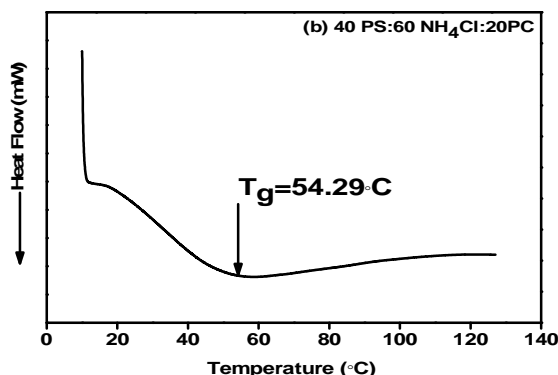


Fig. 2.(b) DSC thermogram of 40 PS: 60 NH₄Cl:20PC biopolymer electrolyte

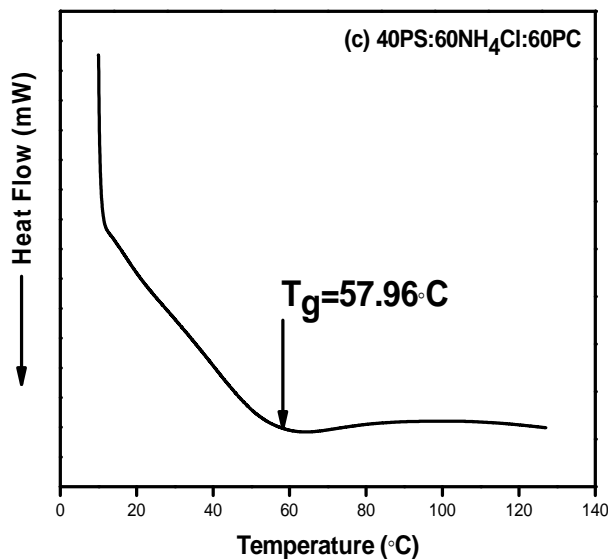


Fig. 2.(c) DSC thermogram of 40 PS: 60 NH₄Cl-60PC biopolymer electrolyte

C. Concentration-Dependent Conductivity

The conductivity (σ) is related to the number of charge carriers (n_i) and their mobility (μ_i) according to the following equation:

$$\sigma = \sum n_i q_i \mu_i \text{----- (2)}$$

Where q_i is the charge on each charge carrier.

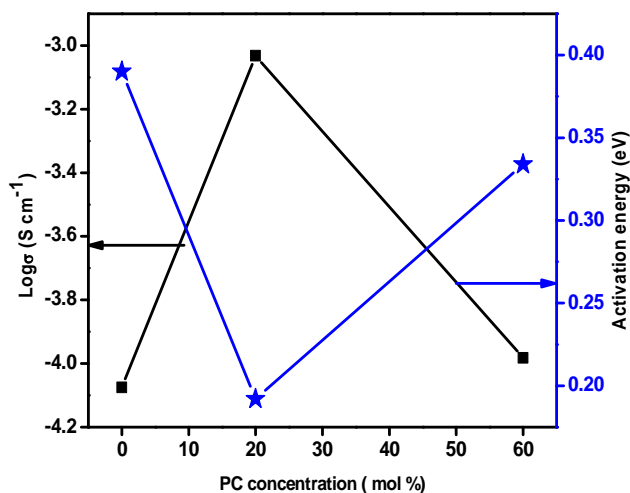


Fig. 3 Variation of conductivity and activation energy as a function of PC Concentration

Figure.3.represents the ionic conductivity of polymer electrolytes and activation energy as a function of PC concentration of the unplasticized and plasticized biopolymer electrolytes. It has been observed that the ionic conductivity of the biopolymer electrolytes increases with increase in propylene carbonate concentration. The reason may be that the addition of plasticizer to the salted-Potato starch films, has helped to dissociate the salt NH₄Cl into mobile proton. The decrease in conductivity value at higher PC concentration (60 mol %) can be explained by aggregation of the ions, leading to the formation of proton cluster, thus decreasing the number of mobile charge carriers and hence the mobility [6]. On Our sample 40 PS: 60 NH₄Cl: 20 PC has got activation energy as 0.192 eV. The lowest activation energy (0.192eV) of 40 PS: 60 NH₄Cl:20 PC among the prepared polymerelectrolytes is due to

decrease in the energy barrier of the proton transport. The variation of the conductivity with propylene carbonate concentration is the outcome of specific interactions between the salt (NH_4Cl), plasticizer (PC) and polymer matrix (PS)^[7].

IV. CONCLUSIONS

The plasticized biopolymer electrolytes 40PS:60 NH_4Cl : X PC (X=0,20,60 mol%) have been prepared by Solution Casting Technique. The X-ray diffraction confirms the amorphous nature of the prepared plasticized biopolymer electrolytesample. DSC analysis shows that the decrease in glass transition temperature (T_g) of Plasticizer Propylene carbonate doped bio polymer electrolytes. The highest ionic conductivity sample (40PS:60 NH_4Cl :20PC) has the lowest activation energy 0.19eV Which is suitable for Fuel cells.

V. ACKNOWLEDGMENT

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