



## **Morphological and Electrical Studies Of Plasticized Biopolymer Electrolytes Based On Potato Starch : NH<sub>4</sub>Cl**

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**Abstract :** Plasticized biopolymer electrolytes based on the “Potato Starch have been prepared using distilled water as solvent by Solution Casting Technique. 40 PS: 60 NH<sub>4</sub>Cl: 20PC biopolymer electrolyte has the maximum ionic conductivity  $9.27 \times 10^{-4}$  S/cm at 303 K. Modulus spectroscopy studies are important to bring out the electrode-electrolyte interfacial behavior and its bulk properties. The SEM images evidenced the presence of numerous pores in the 40 PS: 60 NH<sub>4</sub>Cl: 20PC biopolymer electrolyte resulting in high ionic mobility that leads to high ionic conductivity at ambient temperature.

**Keywords :** Biopolymer, Potato Starch, PC, SEM, Cole-Cole, Modulus.

### **Introduction**

Biopolymers such as Corn Starch, Potato Starch, Banana Starch and Arrow Root Starch etc., are an eco-friendly and harmless polymers. Several factors such as soaring oil prices, worldwide interest in renewable resources, growing concern regarding greenhouse gas emissions and a new emphasis on waste management have created renewed interest in biopolymers<sup>[1]</sup>. Utilization of plasticizers such as Propylene Carbonate (PC), Ethylene Carbonate (EC), Dimethyl Carbonate (DMC), Diethyl Carbonate (DEC) etc., is the effective and efficient method to enhance the ionic conductivity of the biopolymer electrolytes. PC is one of the organic, colorless and odorless organic compound. It has many unique characteristics like highly polar, high dielectric constant (64.9) and aprotic organic solvent<sup>[2]</sup>. In the present study, an attempt has been made to enhance the ionic conductivity of 40 PS and 60 NH<sub>4</sub>Cl by incorporating the plasticizer propylene carbonate in different molar ratios. The prepared plasticized biopolymer electrolytes have been subjected to different studies.

### **Experimental Procedure**

#### **Sample Preparation**

Bio Polymer Potato Starch (PS) with molecular weight= 162.14 g/mol (LOBA CHEMIE), NH<sub>4</sub>Cl with molecular weight= 53.49 g/mol (REACHEM) and PC with molecular weight= 102.09 g/mol (AR grade Merck)

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are used in the Present work. Water solutions of Potato starch and  $\text{NH}_4\text{Cl}$  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 mixture. The obtained mixture is casted in Propylene pertridish and is subjected to vacuum dried at  $40^\circ\text{C}$  for 1 day. Mechanically strong, transparent and flexible films have been obtained.

## Characterization

### Morphological Analysis:

The surface morphology of the polymer electrolytes has been examined with JEOL.JSM-6390 scanning electron microscope.

### 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.

## Results and Discussion:

### Scanning Electron Microscope Studies:

The SEM image of 40 PS: 60  $\text{NH}_4\text{Cl}$  unplasticized and 40 PS: 60  $\text{NH}_4\text{Cl}$ : 20 PC Plasticized biopolymer electrolytes have been shown in Figure.1.(a,&b)

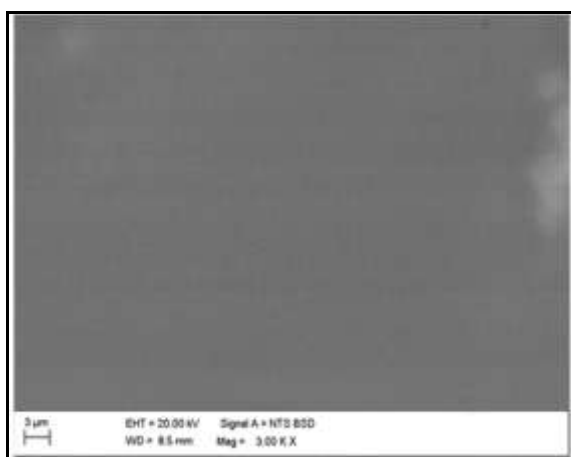


Figure.1.(a) SEM image for 40 PS: 60  $\text{NH}_4\text{Cl}$  unplasticized biopolymer electrolyte

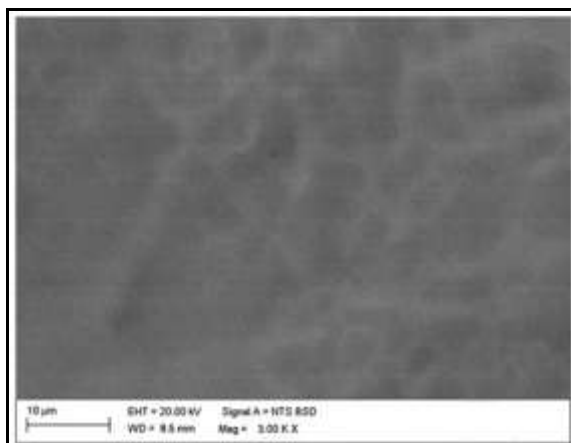


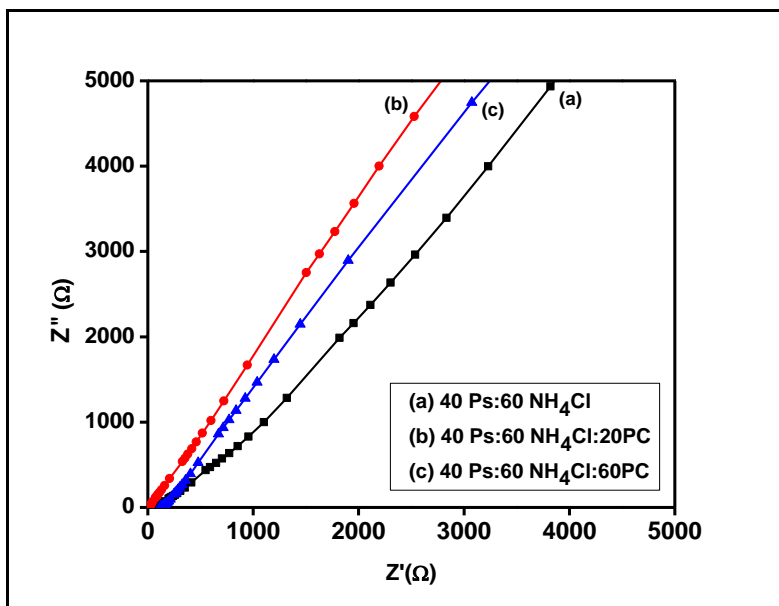
Figure.1(b) SEM image for 40 PS: 60  $\text{NH}_4\text{Cl}$ :20PC plasticized biopolymer electrolyte

The surface morphology of the unplasticized biopolymer electrolyte appears smooth and homogenous. After adding the plasticizer PC to the unplasticized biopolymer electrolyte, the surface becomes rough and uneven. There is also an appearance of pores in the plasticized biopolymer electrolytes as shown in Figure.1.(b). This suggests that the presence of Propylene Carbonate PC will lead to ion mobility resulting in higher ionic conductivity.

**AC Impedance Spectroscopy Analysis**

**Complex Impedance analysis:**

AC impedance spectroscopy is a powerful experimental tool to characterize the electrical properties of polymer materials. The complex impedance plot for all plasticized 40 PS: 60 NH<sub>4</sub>Cl: X PC (X =0, 20, 60 mol% ) biopolymer electrolytes at ambient temperature is shown in figure.2.



**Fig.2. Complex Impedance plot for all Plasticized biopolymer electrolytes at 303 K**

The plot consists of a low frequency spike. The spike may be due to the effect of the blocking electrodes [3]. The intercept of the spike with the real impedance (Z') axis gives the bulk electrical resistance (R<sub>b</sub>) of the biopolymer electrolytes. The ionic conductivity (σ) of the biopolymer electrolytes has been calculated using the equation,

$$\sigma = l / A R_b \dots\dots\dots (1)$$

Where *l* and *A* are the thickness and area of the biopolymer electrolyte respectively[4]. The highest ionic conductivity at ambient temperature has been found to be 9.27×10<sup>-4</sup>S cm<sup>-1</sup> for 40 PS : 60 NH<sub>4</sub>Cl :20 PC polymer electrolyte.

**Table.1. Ionic conductivity values of PS – NH<sub>4</sub>Cl-PC biopolymer electrolytes at different temperatures**

Composition (mol%)	Ionic conductivity(σ) for different composition of PS:NH <sub>4</sub> Cl:PC (S cm <sup>-1</sup> )		
	303K	313K	323K
40PS:60 NH <sub>4</sub> Cl:0PC	8.41×10 <sup>-5</sup>	3.70×10 <sup>-4</sup>	4.0×10 <sup>-4</sup>
40PS:60 NH <sub>4</sub> Cl:20PC	9.27×10 <sup>-4</sup>	1.11×10 <sup>-3</sup>	1.72×10 <sup>-3</sup>
40PS:60 NH <sub>4</sub> Cl:60PC	1.04×10 <sup>-4</sup>	1.89×10 <sup>-4</sup>	1.99×10 <sup>-4</sup>

The incorporation of the plasticizer PC, the conductivity value of 40 PS: 60 NH<sub>4</sub>Cl biopolymer electrolyte increases from 8.41×10<sup>-5</sup> Scm<sup>-1</sup> to 9.27×10<sup>-4</sup>S cm<sup>-1</sup>. The apparent roles of a plasticizer PC in a host

polymer Potato starch are to decrease viscosity of the electrolyte and assist in the dissociation of the salt  $\text{NH}_4\text{Cl}$  which in turn enhances the number of charge carriers<sup>[5]</sup>. The ionic conductivity of the biopolymer electrolyte increases with rise in temperature as shown in table.1. It indicates that the prepared plasticized biopolymer electrolytes are temperature dependent<sup>[6]</sup>.

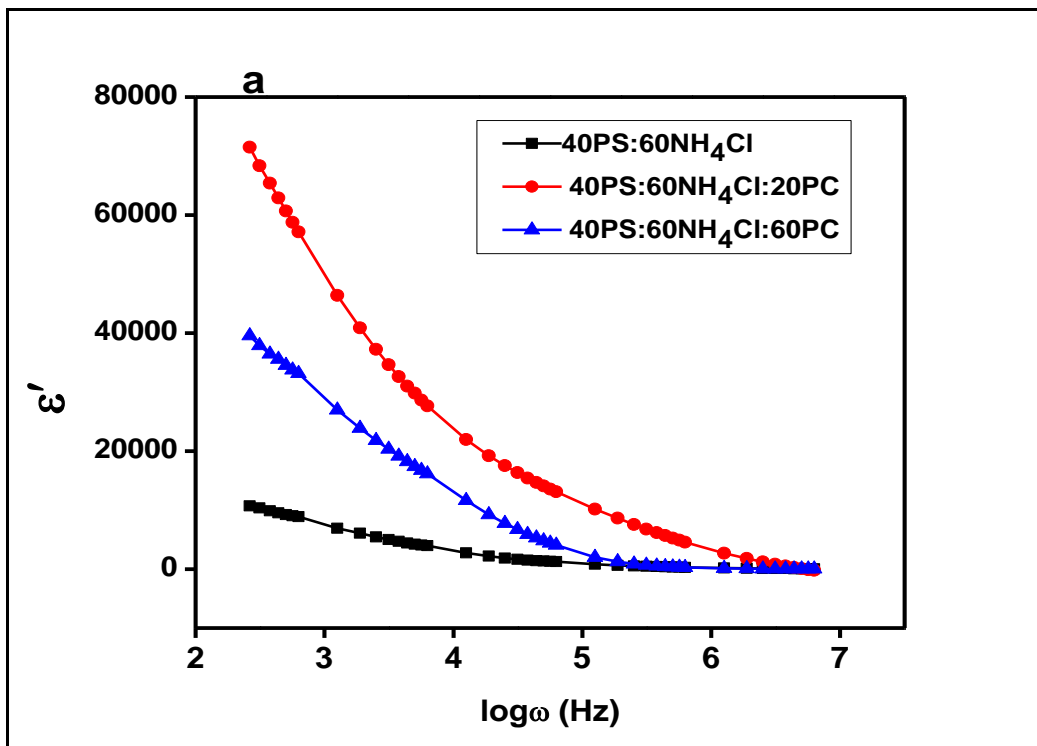
### Dielectric Spectra Analysis

The dielectric behavior of any polymeric system may be reported by the real and imaginary parts of the complex permittivity ( $\epsilon^*$ ) and is defined by the relation:

$$\epsilon^* = \epsilon'(\omega) - i \epsilon''(\omega) \text{-----(2)}$$

Where  $\epsilon'(\omega)$  &  $\epsilon''(\omega)$  are the real and imaginary components of the permittivity respectively. These components represent the energy storage and energy loss in each cycle of the applied electric field respectively.

The values of dielectric constant which is the representation of energy storage ( $\epsilon'$ ) and dielectric loss which is the representation of energy loss ( $\epsilon''$ ) are very high at low frequencies and relatively constant at higher frequencies indicates that the presence of the plasticizer PC may result in more localization of charge carriers along with mobile ions leading to high ionic conductivity<sup>[7]</sup>. In the high frequency region, the periodic reversal of the applied electric field is so high that the dipoles are unable to follow the applied electric field and hence there is no excess ion diffusion in the field direction resulting in the decrease in dielectric constant<sup>1</sup>. High values of  $\epsilon'$  and  $\epsilon''$  at low frequencies have been obtained for the plasticized biopolymer electrolytes than the unplasticized one. It suggests the presence of enhanced charge carrier density in the space charge region<sup>[8]</sup>



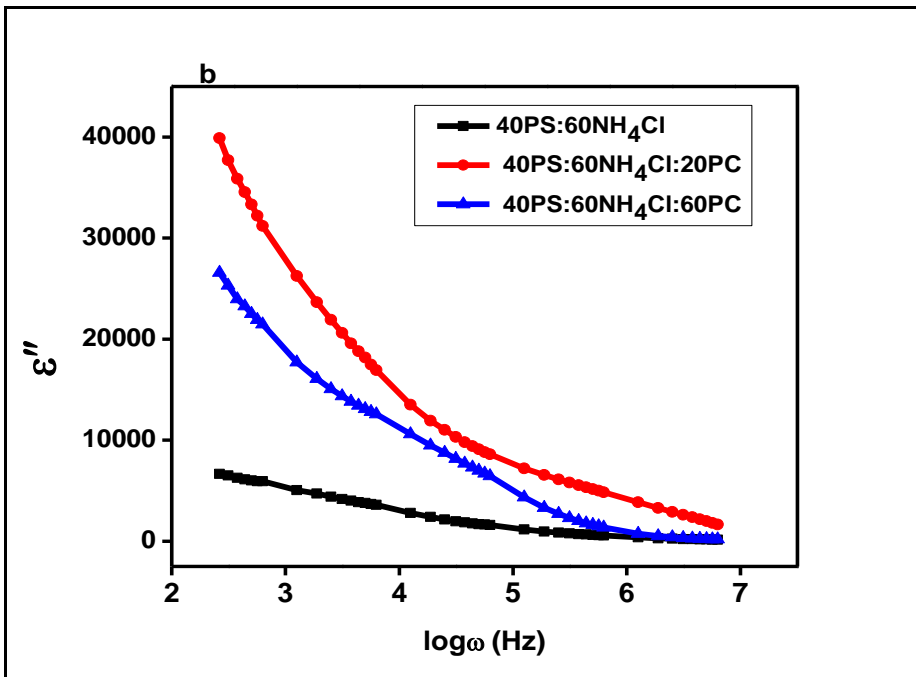
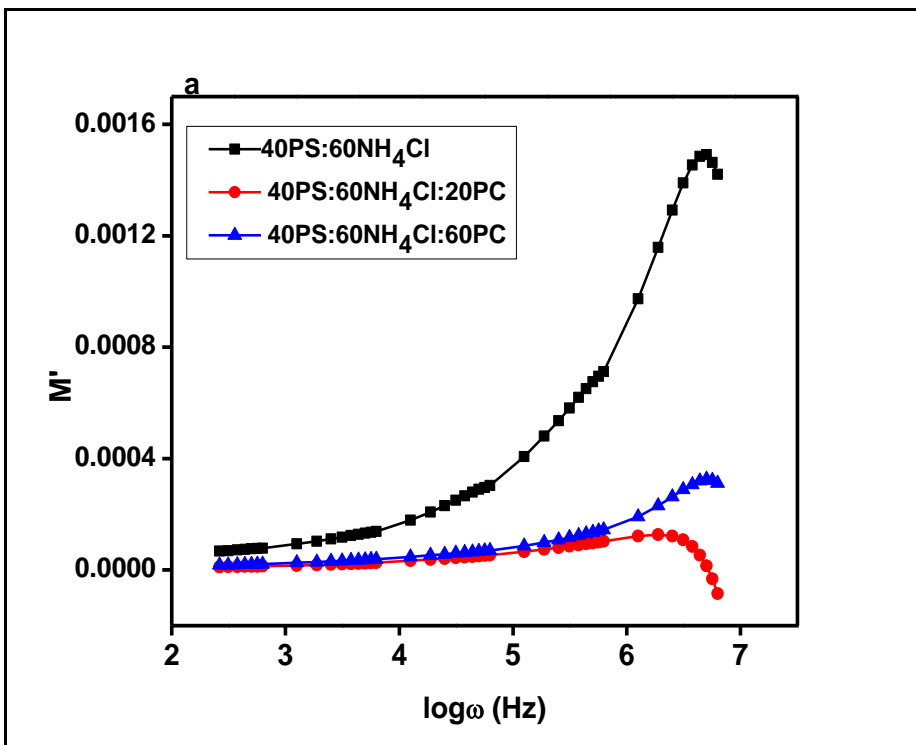


Figure.3 (a & b) Dielectric constant and Dielectric loss spectra of all plasticized bioPolymer electrolytes at 303 K

Electrical Modulus Studies:



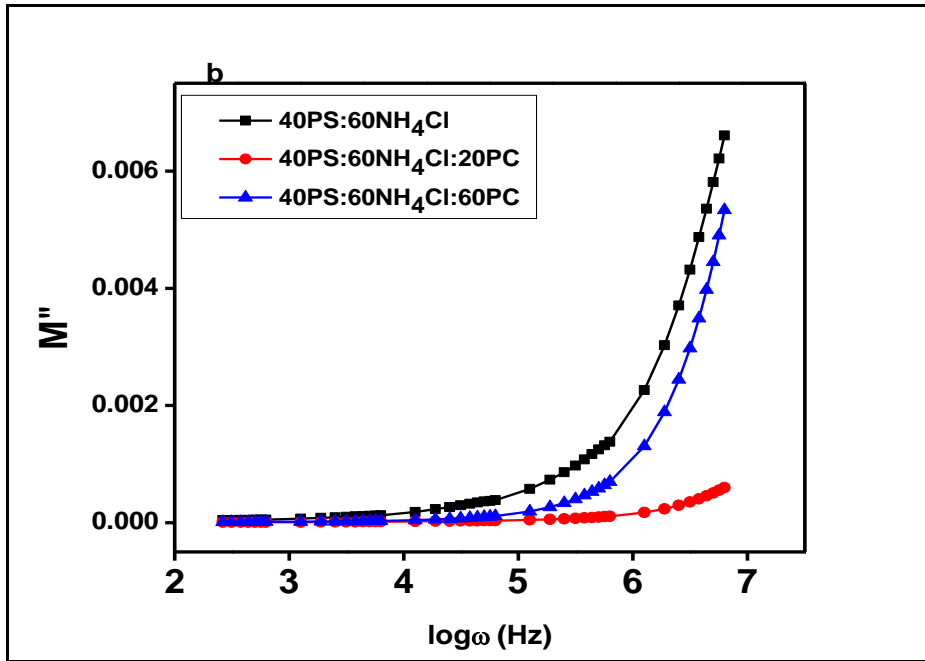


Figure. 4 .(a & b)Frequency dependence of  $M'(\omega)$  and  $M''(\omega)$  of all plasticized bio Polymer electrolytes at 303K

Macedo et al.<sup>[9]</sup> have presented the electric modulus  $M$  in order to overcome the effect of electrode polarization. Modulus spectroscopy studies are important to bring out the electrode-electrolyte interfacial behaviour and its bulk properties. The electric modulus is defined as,

$$M^* = M' - jM'' \text{----- (3)}$$

where  $M'$  and  $M''$  are real and imaginary part of the complex electric modulus respectively.

Figure.3 (a&b) depict the frequency dependence of  $M'(\omega)$  and  $M''(\omega)$  of all Plasticized biopolymer electrolytes at 303K respectively. Both plots show an increase and well-defined dispersion peaks in the high frequency end. This may be due to the bulk effect. The height of the peak in the electrolytes decreases with the raise of temperature, suggesting a plurality of relaxation mechanism. At lower frequencies, there is a long tail in both the plots. It indicates the negligible contribution of electrode polarization<sup>[10]</sup>.

**Conclusion:**

40PS:60 NH<sub>4</sub>Cl and 40PS:60 NH<sub>4</sub>Cl: X PC (X=0, 20, 60 mol%) proton conducting Bio polymer electrolytes have been prepared by Solution Casting Technique. The SEM images evidenced the presence of numerous pores in 20 mol% PC added biopolymer electrolyte resulting in high ionic mobility that leads to higher ionic conductivity. 40 PS: 60 NH<sub>4</sub>Cl: 20PC bio polymer electrolyte has the maximum ionic conductivity  $9.27 \times 10^{-4} \text{ S/cm}$  at 303 K. The value of both  $M'$  and  $M''$  tends to be zero in the vicinity at lower frequencies which suggests the suppression of the electrode polarization at interface.

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