Journal of Applied Science and Engineering Methodologies
Volume.2, No.3, (2016): Page.336-341
www.scientistlink.com/jasem

# Polymer Crust Electrolyte Based On Starch-Chitosan Blend Mixed With KI by Gelation Method

**E. BEMENTA[1], M.A. JOTHI RAJAN[2*]**

[1, 2*] *PG & Research Department of Physics, Arul Anandar College (Autonomous), Karumathur, Madurai, India -625514*
*bementa88@gmail.com, majothirajan58@gmail.com*

**ABSTRACT**

*The usage of biopolymer materials in the polymer crust electrolyte system helps to abolish environmental crisis, which will unswervingly carry towards green nation with good ionic conductivity. Biodegradable polymer crust electrolyte based on starch chitosan blends mixed with potassium iodide has been developed through gelation method. This work has the details of conductivity, dielectric, dielectric loss tangent, and modulus measurements. The decrease in diameter of the semicircle in Nyquist plots proved the increase in conductivity of polymer crust. Impedance analysis shows that the entire sample has gel like conductivity. The room temperature conductivity of electrolyte of 4.6544 x $10^{-4}$ was enhanced to 1.5405 x $10^{-2}$ S/cm on addition of 6 weight percentages of potassium iodide, affirming the increase in the number of charge carriers. The value of dielectric constant was low in higher frequency side and high at low frequency side. The height of the hump decreased from the addition of 1 to 6 weight percentages of KI. The long range motion of mobile charge carrier and conduction in material are indicated by the peak shift towards high frequency end. The long tail obtained in the modulus plot depicts the crust as an ionic conductor.*

**KEY WORDS**

*Gel polymer electrolyte, Starch-chitosan blend, Potassium iodide, Conductivity, Conduction mechanism*

## 1. INTRODUCTION

Today the ionic conductivity of electrolyte in electrochemical devices is high due to the replacement of synthetic materials. As it was harmful and non-biodegradable, it was considered hazardous to the environment and human [1]. The progress of polymeric system with high ionic conductivity was one of the main objectives in polymer research [2]. Many methods were recommended for enhancing the ionic conductivity such as copolymerization [3], polymer blending [4], incorporation of ceramic fillers [5] and plasticization [6]. Polymer blending can improve the mechanical properties and biocompatibility of blend components. It is well known that mixing of polymer is an effective and well-suited method to improve the performance of polymeric materials [7]. Gel formation techniques are very popular now-a-days. It was recommended for an approach to conquer high conductivity value close to that of liquid electrolytes [8]. On account of properties like high ionic conductivity and good adhesion, gel electrolytes have priority than conventional polymer electrolytes [9].

Some polysaccharides possess great capability like good mechanical and adhesion properties being processed in the crust form. In addition they are easily obtained from renewable and biodegradable sources and are cost effective [10]. Starch catches the attention of scientists because of its rich variety and abundance in nature. It is composed of repeating 1,4-α D glucopyranosyl units, amylase and amylopectin[11], and chitosan consists of β-1,4 linked 2-amino deoxy-D glucopyranose that can be prepared by deacetylation of chitin [12]. The blend of starch and chitosan was reported to form mechanically stable crust due to inter and intra molecular hydrogen bond that is created between the hydroxyl and amino group of starch and chitosan [13]. In the present paper an endeavour has been made to investigate blend polymer crust. This paper reports the ionic conductivity and dielectric study of potassium iodide incorporated into starch –chitosan blend.

## 2. EXPERIMENTAL

Starch $(C_6H_{10}O_5)n$ was purchased from Merk , Chitosan low molecular weight was purchased from Sikma Aldrich,and potassium iodide extra pure was purchased from S.d Fine-CHEM LIMITED, Mumbai. 1.66 weight percentage (wt %) of starch solutions were prepared. It was heated at 80 $^{o}$ C. The as prepared starch solution was left to cool down to room temperature. Another 1.66 wt% of chitosan solution were prepared separately.

Published by SLGP. Selection and/or peer-review under responsibility of ICISEM 2016. Open access under CC BY-NC-ND license.

The chitosan solution was added drop wise to the starch solution and stirred till a homogeneous solution was obtained. For the preparation of salted system, different amounts of KI was dissolved in 5 ml of double distilled water and added to the starch-chitosan solution and stirred until complete dissolution was achieved. All homogeneous solutions were poured into glass petri dishes and were left to dry. The dried crust was then kept in desiccators, for avoiding any trace of moisture.

## 3. IMPEDANCE SPECTROSCOPY

The impedance of the films was measured using Princeton applied research model Versa STAT MC in the frequency range of 1 Hz to 1 MHz at room temperature. The electrolyte film was sandwiched between two stainless steel electrodes. A small sinusoidal potential was applied and current through the sample was measured. The impedance was measured for every operating frequency using the data [14].

### *3.1 Conductivity Measurement*

The ionic conductivity of the samples was calculated using the following formula

$$\sigma = t/R_b \times A \text{ S/cm} \quad \ldots\ldots\ldots\ldots\ldots (1)$$

where σ is the conductivity (S/cm), ($R_b$) is the bulk resistance obtained from Nyquist plots. t is the thickness of sample (cm), and A is the area of the given sample ($cm^2$) [15]. The calculated values of conductivity are plotted in Fig.1, and listed in Table 1

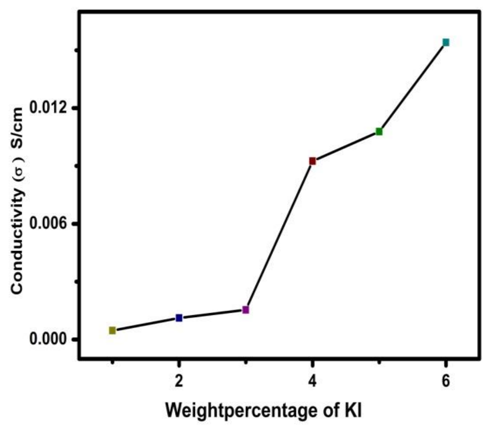


**Fig.1:** Effect of KI on starch-Chitosan blend matrix

**Table1**: Conductivity of starch-chitosan blend mixed with KI solution for polymer crust electrolyte system at room temperature.

| Sample code | Starch wt % | Chitosan wt % | Composition (wt% of KI) | σ (S/cm) |
|---|---|---|---|---|
| SC1 | 1.6 | 1.6 | 1 | $4.6544 \times 10^{-4}$ |
| SC2 | 1.6 | 1.6 | 2 | $1.12046 \times 10^{-3}$ |
| SC3 | 1.6 | 1.6 | 3 | $1.15404 \times 10^{-3}$ |
| SC4 | 1.6 | 1.6 | 4 | $9.2516 \times 10^{-3}$ |
| SC5 | 1.6 | 1.6 | 5 | $1.0788 \times 10^{-2}$ |
| SC6 | 1.6 | 1.6 | 6 | $1.5405 \times 10^{-2}$ |

From Table 1 and Fig. 1, one can understand that addition of KI in starch-chitosan blends enhanced the ionic conductivity. It had happened due to creation of more mobile ions in starch-chitosan blend matrix and due to the addition of KI which enhanced the overall conductivity. The highest conductivity is optimized at $1.5405 \times 10^{-2}$ (S/cm) with the addition of 6 wt % KI. Linear increments in conductivity are an ample proof for the complete dissolution of salt. The increase in conductivity with KI is attributed due to the amount of ions in the polymer electrolyte which increase with increase in KI concentration [16]. This had happened the starch and chitosan have ether oxygen, this ether oxygen can easily get associated with cation (K+), the weakly bound K+ ions can hop together with I $^-$ consistently coordinating side of the starch chitosan blend, thereby increasing conductivity.

*3.2 Dielectric Studies*

The dielectric study of biopolymer electrolyte are very useful in the study of conductivity behaviour in biopolymer electrolyte .The variation on ε' and ε" with varying composition in wt% of KI salt is shown in Figure 2(a) and 2(b), respectively. The values of ε' and ε" are calculated by using the following relations:

$$\varepsilon' = Z''/(C\,\omega(Z'^2 + Z''^2)) \quad .............. (2)$$

$$\varepsilon'' = Z'/(C\,\omega(Z'^2 + Z''^2)) \quad .............. (3)$$

where $C=\varepsilon_0 A/t$. Z' and Z" are the real and imaginary parts of the impedance, ω is the angular frequency, C is the capacitance of empty measuring cell of electrode with area A, $\varepsilon_0$ is the dielectric constant, and t is the thickness of the biopolymer film [17].

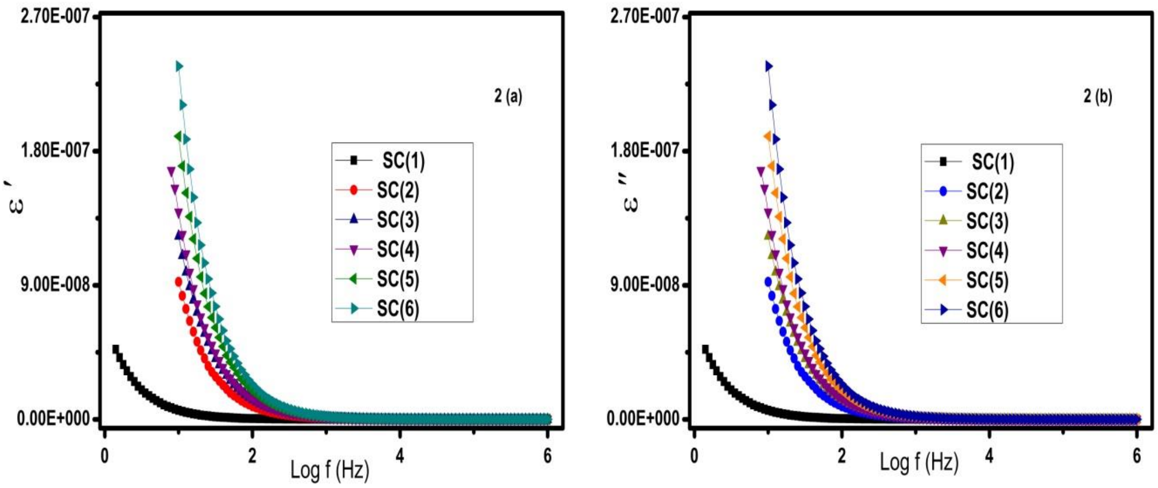


**Fig.2(a):** Frequency dependence of **ε'** for starch –chitosan mixed with KI, and **Fig.2(b):** Frequency dependence of **ε"** for starch –chitosan mixed with KI.

The addition of KI solution results in the change in the dielectric constant of the matrix at lower frequencies. The conductivity was mainly due to the change in the number of free charge carriers. The spectra consist of two well defined regions, a low frequency dispersive region due to electrode polarization effects and the plateau representing the ionic conductivity. At low frequencies, the ionic conductivity is high enough to produce a significant build up of charges at the electrodes which reduces the effective applied field and hence the conductivity. [18].

*3.3 Dielectric Loss Tangent*

For a better understating of dielectric phenomena and conducting behaviour, we have calculated the dielectric loss tangent given by the following relations:

$$\tan\delta = \varepsilon''/\varepsilon' ................. (4)$$

where ε' and ε" are the real and imaginary parts of dielectric constant of biopolymer electrolyte. Fig.3. shows a big hump towards the higher frequency region which is also supported by our conductivity data. The loss spectra characterized by peak appearing at a characteristic frequency of starch-chitosan mixed KI films suggest the presence of relaxing dipoles in all the biopolymer electrolyte film [19]. The frequencies of relaxation depend on the characteristic property of dipole relaxation. The tangent loss peaks shift toward the high-frequency side of increased wt % of KI concentration. This is an ample proof for the migration of ions [20].

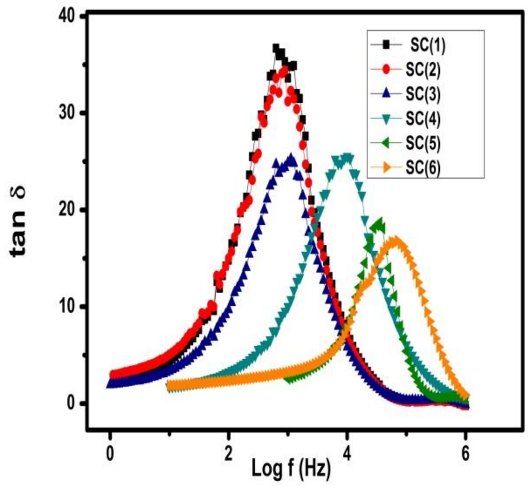


**Fig.3:** The dielectric loss tangent calculated at various frequencies for starch –chitosan mixed with KI.

*3.4 Dielectric Modulus*

Dielectric modulus had been calculated to analyze the different relaxation phenomena in the biopolymer electrolyte system. The modulus was calculated by the following equations:

$$M^* = 1/\varepsilon^* = M' + i\, M'' \quad \text{.......................} \quad (5)$$

where M' is the real dielectric modulus and M" is the imaginary dielectric modulus, also

$$M' = \varepsilon'/ (\varepsilon'^2+\varepsilon''^2) \quad \text{........................} \quad (6)$$

$$M'' = \varepsilon''/ (\varepsilon'^2+\varepsilon''^2) \quad \text{........................} \quad (7)$$

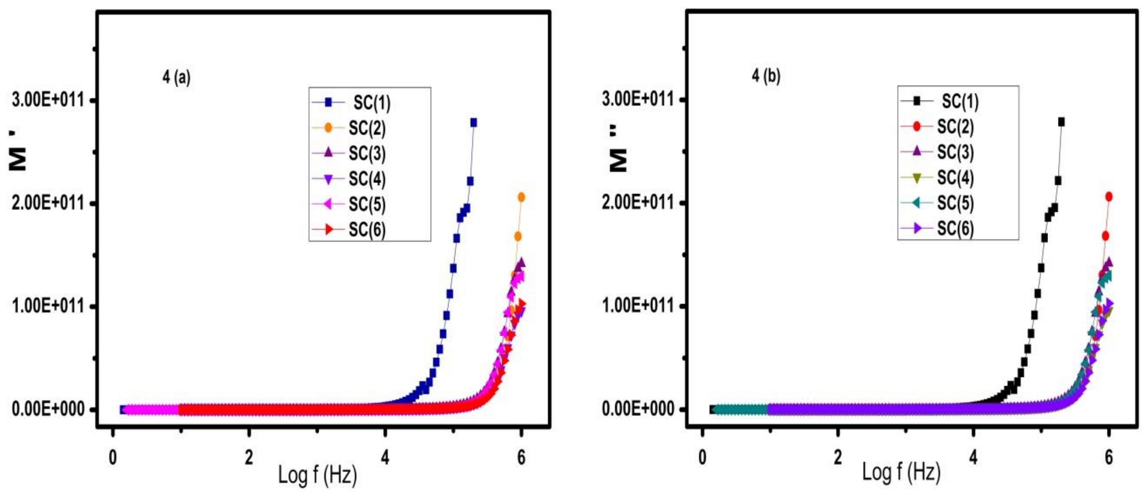


**Fig.4(a):** Frequency dependence of M' for starch –chitosan mixed with KI and **Fig.4(b):** Frequency dependence of M" for starch –chitosan mixed with KI.

From Fig. 4(a) & 4(b), it is clear that both M' and M", the value of dielectric modulus increase at the higher frequency end and exhibit a long tail feature at low frequency end. This indicates that the material is very capacitive in nature. The presence of peak in the modulus formalism at higher frequencies for all polymer systems is an indicator that the polymer crust electrolytes are ionic conductors [21, 22].

## 4. CONCLUSION

Starch-chitosan blends based polymer crust electrolyte mixed with KI was successfully prepared by gelation method. Complex impedance spectroscopy shows that ionic conductivity was enhanced by mixing of low weight percent of KI in starch-chitosan blend. Dielectric modulus showed long tail feature and was due to high capacitance. Hence electrolyte films can be used as safer separator in electrochemical devices.

### ACKNOWLEDGEMENTS

The authors gratefully acknowledge PG and Research Department of Physics, Arul Anandar College, Karumathur, Madurai, (India) for providing the facility to do experimental work.

## REFERENCES

[1] R. Singh, N.A. Jadhav, S. Majumder, B. Bhattacharya and P.K. Singh, Novel biopolymer gel electrolyte for dye-sensitized solar cell application, Carbohyd. Polym, 91, 2013, 682-690.
[2] Y.S. Zhu, X.J. Wang, Y.Y. Hou, X.W. Gao, L.L. Liu, Y.P. Wu, and M. Shimizu, A novel gel polymer electrolyte based on poly ionicliquid1-ethyl 3-(2-methacryloyloxy ethyl) imidazolium iodide, European Polymer Journal, 43, 2007, 2699–2707.
[3] Kamlesh Kumari and Usha Rani, Controlled Release of Metformin hydrochloride through crosslinked blends of chitosan-starch, Advances in Applied Science Research, 2 (2), 2011,48-54.
[4] Thawien Bourtoom, Manjeet S. Chinnan, Preparation and properties of rice starch chitosan blend biodegradable film, LWT - Food Science and Technology, 41, 2008, 1633-1641.
[5] Tanmaya Badabanda,Ranjankumar and Harichandan, , Frequency and temperature dependence behaviour of impedance, modulus and conductivity of $BaBi_4Ti_4O_{15}$ Aurivillius ceramic, Processing and Application of Ceramics, 8, 2014, 145-153.
[6] M.F Shukur, and M.F.Z.Kadir, Electrical and transport properties of NH4Br-doped cornstarch-based solid biopolymer electrolyte, Ionics 12, 2014, 224-238.
[7] Y.N. Sudhakar, and M. Selvakumar, Lithium perchlorate doped plasticized chitosan and starch blend as biodegradable polymer electrolyte for super capacitors, Electrochimica Acta, 78, 2012, 398-405.
[8] Jae-Kwang Kim, Cho-Rong Shin, Jou-Hyeon Ahn, Aleksandar Matic, and Per Jacobsson, Highly porous LiMnPO4 in combination with an ionic liquid-based polymer gelelectrolyte for lithium batteries, Electrochemistry Communications, 13, 2011, 1105–1108.
[9] M.F. Shukur and , M.F.Z. Kadir, , Hydrogen ion conducting starch-chitosan blend based electrolyte for application in electrochemical devices, Electrochimica Acta, 158, 2015, 152-165.
[10] S.R. Majid, and A.K. Arof, Proton-conducting polymer electrolyte films based on chitosan acetate complexed with NH4NO3 salt, Physica B, 355, 2005, 78–82.
[11] A. S. Ahmad Khiar & A. K. Arof, Conductivity studies of starch-based polymer electrolytes, Ionics, 16, 2010,123–129.
[12] Z. Osman, Z.A. Ibrahim, and A.K. Arof, Conductivity enhancement due to ion dissociation in plasticized chitosan based polymer electrolytes, Carbohydrate Polymers, 44, 2001, 167–173.
[13] Mewada R. K., Nimish Shah and Mehta Tejal., Synthesis of covalently crosslinked chitosan-starch copolymers through reactive blending for oral drug delivery, Journal of Environmental Research And Development, 9, 2015, 1133-1137.
[14] Jeremy, C. H. Koh, Zainal Arifin Ahmad,Ahmad and Azmin Mohamad, Bacto agar-based gel polymer electrolyte, Ionics, 18,2012, 359–364.
[15] J. F. Du, Y. Bai, W. Y. Chu, and L. J. Qiao, The Structure and Electric Characters of Proton-Conducting Chitosan Membranes with Various Ammonium Salts as Complexant, Journal of Polymer Science: Part B: Polymer Physics, 48, 2010, 880–885.
[16] A. K. Arof, S. Amirudin, S. Z. Yusof and I. M. Noor, A method based on impedance spectroscopy to determine transport properties of polymer electrolytes, Phys. Chem. Chem. Phys, 16, 2014, 1856-1867.
[17] N. H. Idris H. B. Senin and A. K. Arof, Dielectric spectra of LiTFSI-doped chitosan/PEO blends, Ionics, 13, 2007, 213–217.

[18] J. Einfeldt, D. Meibner, and A. Kwasniewski, Contributions to the molecular origin of the dielectric relaxation processes in polysaccharides – the high temperature range, Journal of Non-Crystalline Solids, 320, 2003, 40–55.
[19] Rahul Singh, Jaya Baghel, S. Shukla, and B. Bhattacharya, Hee-Woo Rhee and Pramod K. Singh, Detailed electrical measurements on sago starch biopolymer solid electrolyte, Phase Transitions, 2014, 1-9
[20] M. F. Shukur, R. Ithnin, and M. F. Z. Kadir, Electrical properties of proton conducting solid biopolymer electrolytes based on starch– chitosan blend, Ionics, 20, 2014, 977–999
[21] A.S.A. Khiar, R. Puteh, and A.K. Arof , Conductivity studies of a chitosan-based polymer electrolyte Physica B, 373, 2006, 23–27
[22] Sit Y.K., Samsudin A.S. and Isa M.I.N, Ionic Conductivity Study on Hydroxyethyl Cellulose (HEC) doped with NH4Br Based Biopolymer Electrolytes, Research Journal of Recent Sciences, 1[11], 2012, 16-21.