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Electrical transport behaviour of bio-polymer electrolyte system: Potato starch + ammonium iodide

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ABSTRACT

A new bio-polymer electrolyte system is prepared by mixing NH_4I with potato starch. Prepared material is an ionic conductor having ionic transference number (t_{ion}) ~0.95 and ambient electrical conductivity $\sim 2.4 \times 10^{-4}$ S/cm. Relation between the conductivity trend, mobile ion concentration factor (K) and mobility factor (μ_f) with respect to salt concentration and temperature, is established. The optical micrograph of starch + NH_4I system indicated typical starch–iodine relationship in acidic medium. In conductivity formulism three different regions for power law exponent (n) having values between $0 < n < 2$ is found. The regions are associated with dc conductivity, NCL and superlinear like behaviour. In starch electrolyte, NCL region is obtained at room temperature and low frequency region. Material is humidity immune up to 77% relative humidity and a very small variation with temperature has been found hence results are encouraging for possible use of starch based electrolytes in humidity immune devices.

1. Introduction

Solid polymer electrolytes (SPEs) have been the subject of interest due to their potential applications in various technological areas as they have an edge over liquid electrolytes because of being robust (Riess, 2000). Now a day due to lot of peril to our environment, biomaterials are receiving a great attention in every field including electrochemistry. In recent years, the capability of starch to be used as polymer matrix has been recognised. Hence many electrochemists started extensive work in this direction (Finkenstadt & Willett, 2004; Finkenstadt, 2005; Gomes, Ribeiro, Malafaya, Reis, & Chuha, 2001; Ning, Xingxiang, Haihui, & Jianping, 2009; Singh, Bhattacharya, Nagarale, & Rhee, 2010; Van Soest & Borger, 1997). Recently starch became one of the most popular, renewable and biodegradable polymers. Starch attracts scientists because of its rich variety and abundances in nature. It is composed of repeating 1,4-α-D-glucopyranosyl units: amylose and amylopectin; however, the relative amounts of these substances depend upon the plant sources (Avella et al., 2005; Lenz, 1993).

Our group is also working to explore the possibilities of using starch as a polymer host. Starch being direct food, for living things, fungus growth is unavoidable in these materials. Fungus growth is seen in these materials within two to three days of material preparation. A small amount of glutaraldehyde (GA) has been found to restrict the fungal growth and give a soft film of starch (Tiwari, Pandey, Srivastava, & Srivastava, 2011; Tiwari, Srivastava, & Srivastava, 2011). Different starches like arrowroot, corn and potato starches are currently being used (Tiwari, Pandey, et al., 2011; Tiwari, Srivastava, et al., 2011) in our laboratory. Morphology of potato starch is found to be better in comparison to other starches. It results in soft flexible film with high conductivity in comparison to others.

Hydrogen ion conducting polymer materials are very useful for device applications. These materials are developed by doping polymers with acids (Aihara & Sonai, 2006; Fontanella, Wintersgill, Wainright, Savinell, & Litt, 1998) or ammonium salts. Experiments with the acids are undergoing in our laboratory. Initial studies indicated that acids have a tendency to break the starch and it is difficult to get a soft film like material. Ammonium salts do not have such kind of problem. Present paper reports preparation and characterisation of biopolymer electrolyte prepared by mixing potato starch with NH_4I.

2. Experimental

Potato starch (PS) $(C_6H_{10}O_5)_n$ (Loba Chemie, India), NH_4I (Loba Chemie, India), glutaraldehyde (GA) $(C_5H_8O_2)$ (Loba Chemie, India), acetone (M) (RFCL Limited, India) have been used for sample preparation. The materials used were of analytical grade. Polymer films have been prepared by solution cast technique with varying salt concentration of NH_4I (i.e. from 10 to 50 wt%), dissolving the solid

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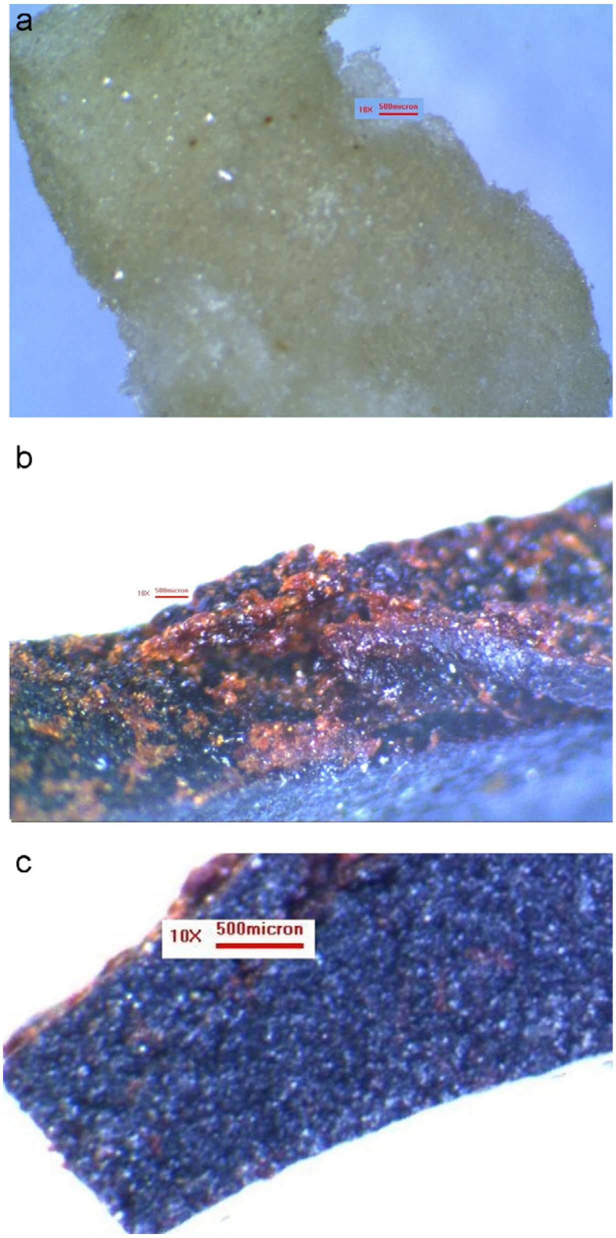

Fig. 1. (a) Micrograph image of starch + NaI system, (b) micrograph image of starch + NH_4I system in vertical and (c) horizontal view.

components in acetone. The obtained solution was stirred on a hot plate magnetic stirrer at 30 °C for 6–8 h to get homogeneous mixture. After that, the solution was poured into a Petri dish (polypropylene dish) and left to evaporate slowly at room temperature for 4–5 days. Resultant is homogenous thick film of material.

Conductivity measurement have been done with Hioki LCR Hi-Tester(3522) in the frequency range from 42 Hz to 5 MHz. Ionic transference number of the material has been evaluated by DC polarisation method using Graphtec XY recorder (WX 3000). Aluminium metal foil has been used as an electrode for the measurement. Micrographs are taken by CatScope CS-SLBX, Catalyst Biotech.

3. Results and discussion

3.1. Optical microscopy

Fig. 1a–c shows the micrographs of “starch + GA” and “starch + GA + 20% NH_4I” systems (vertical and horizontal view). Sample without salt has a yellowish colour where as complexed sample has a mixed blue and yellow portions. Sample was divided into two parts before taking the micrographs. The surface (Fig. 1c) has a dark bluish colour. The inner view or the vertical view of the sample (Fig. 1b) also has dominating bluish colour but with some yellowish portions. Presence of yellowish colour indicates iodine ions are not entered in that portion of starch helix or it indicates amylopectin portion. Amylopectin does not affect colouration property of starch with iodine.

Here we would like to draw the reader’s attention towards our previous studies (Tiwari, Pandey, et al., 2011; Tiwari, Srivastava, et al., 2011). Starch doped with NaI (Tiwari, Pandey, et al., 2011; Tiwari, Srivastava, et al., 2011) results in homogenously yellowish colour film. In present study (starch + NH_4I) bluish colour dominates with a very small yellowish portion. The reason can be elucidated in terms of well understood relation between starch and iodine. Starch is known to give colouration effect in presence of iodine and colour of system varies from yellow to blue depending upon content of starch and/or iodine, medium’s pH etc. (Pimstone, 1962). When three iodine ions go inside the amylose helix and get arranged in a particular linear shape then a blue colour appears which is accentuated in presence of acidic medium and disappears if pH increases.

In view of above, difference in colouration between starch + NaI and starch + NH_4I can be understood in terms of dissociation constants of salts (NaI = 3.16 eV and NH_4I = 2.50 eV) and acidic nature of the salt solutions (pH for NaI = 8.0 and NH_4I = 5.6) (Clifford, 1925). It is obvious that NH_4I can be easily dissociated in comparison to NaI and NH_4I has acidic nature where as NaI has a basic nature. Hence, in case of starch + NaI system we are getting a yellowish colour (because of low concentration of iodine ion and high pH tendency of NaI) whereas in starch + NH_4I system dark blue colour is appearing due to its low dissociation constant and acidic nature of NH_4I.

3.2. Transference number measurement

Ionic transference number is an imperative parameter for electrolytes. It indicates fraction of conductivity due to movement of ions. Total ionic transference number of the prepared material has been measured by dc polarisation method. In this technique, the dc current is monitored as a function of time on the application of a fixed dc voltage (0.5 V) across Al/electrolyte/Al cell. The transference number has been calculated from the polarisation graph using following equation:

$$t_{\text{ion}} = \frac{I_{\text{initial}} - I_{\text{final}}}{I_{\text{initial}}}$$

The calculated transference number is >0.95. It implies that prepared film is mainly ion conducting hence is electrolytic in nature.

3.3. Conductivity study

Conductivity of electrolytes depend upon charge carrier concentration, charge on carrier, and size of carrier. Hence, when charge concentration is changed by doping, then the conductivity is also expected to change. In polymer–salt complexes, charge carrier concentration is not directly proportional to doping concentration of salt which is clearly indicated in ‘σ vs. wt% of salt’ curves of polymer electrolytes.

Fig. 2(a) presents effect of ammonium iodide concentration on conductivity. Conductivity follows the typical trend of polymer–salt complexes. It initially attains a maxima (at 20 wt% of the salt) followed by minima (at 40 wt% of the salt) then again it rises. Many theories explaining the phenomenon can be found in literature. Change in conductivity can be correlated with change

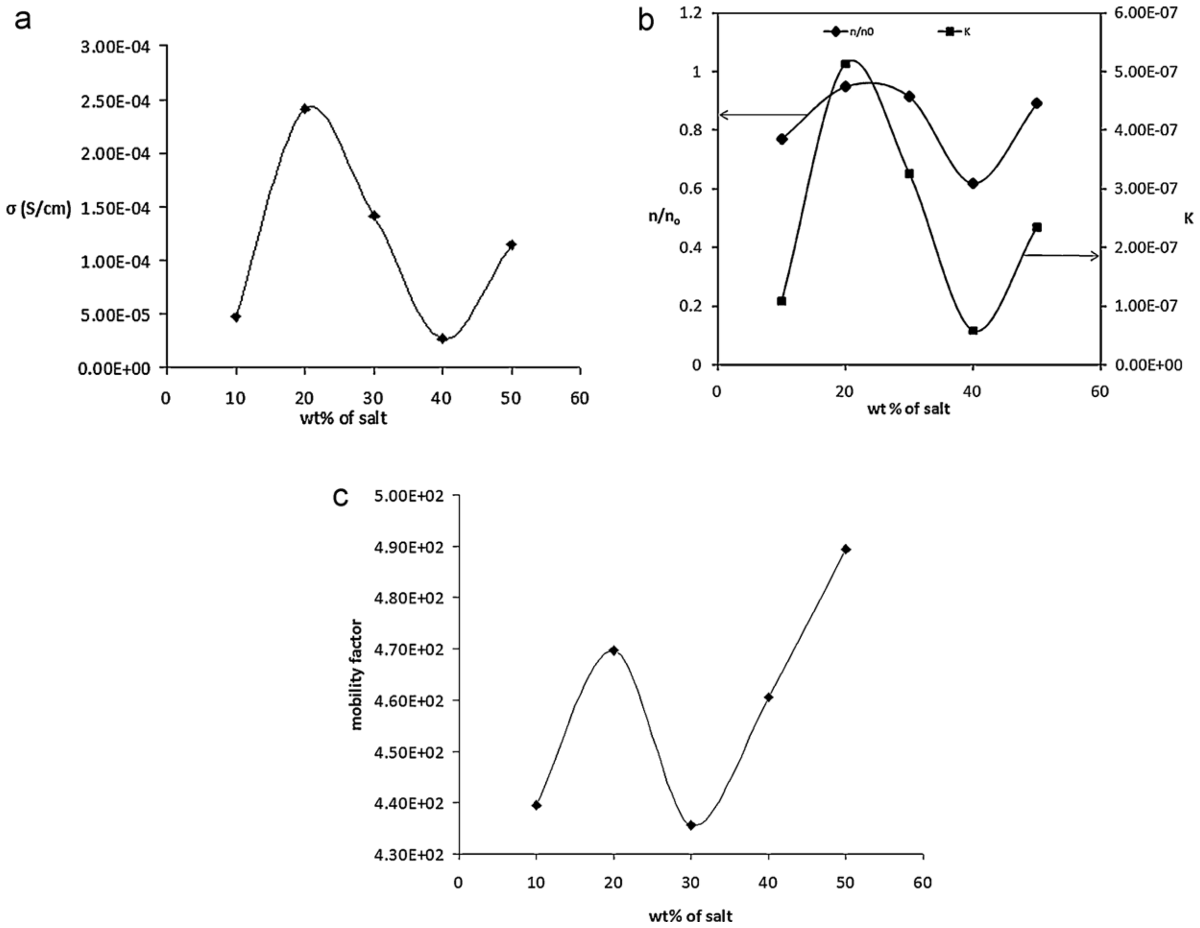

Fig. 2. (a) Variation of conductivity with salt concentration, (b) variation of carrier ion concentration (K) and ion dissociation factor (n/n_0) with wt% of salt, (c) variation of mobility factor (μ_f) with salt wt%.

in charge carrier concentration and/or change in their mobility. To ascertain the origin of conductivity changes in present system, mobile ion concentration factor (K) (Patro & Hariharan, 2011) and mobility factor (μ_f) has been estimated and their variation with respect to added salt concentration has been studied. Fig. 2b and c represents these changes graphically. Effect of salt concentration can also be understood in terms of fractional dissociation (n/n_0) (Bhattacharya, Lee, Geng, Jung, & Park, 2009) of salt as shown in Fig. 2b. Mobile ion concentration data (both mobile concentration factor and dissociated charge fraction) are following conductivity trend. This confirms that ion pair formation and re-dissociation theory applicable to polymer–salt complexes (Fuoss & Kraus, 1933; Grigo, 1982; Kenausis, Evers, & Kraus, 1962; Kenausis et al., 1963) are applicable in the present system also. Ion dissociation factor shows an appreciable change and presents a better picture of phenomenon. Minimum conductivity is associated with the decreased dissociation. Increased ion association (i.e. decreased dissociation) or triplet ion formation both are expected to decrease mobility; one due to electrostatic hindrance in movement and the other one because of increased weight of charge carriers. The same can also be associated with mobility factor decrease. Both mobile ion concentration factor (K) as well as ion dissociation factor (n/n_0) indicate a decreasing trend for the salt concentration of 30 wt% and 40 wt%, but the mobility factor data is showing an increasing trend from 40 wt% of salt (Fig. 2c). The phenomenon may be the consequence of salt plasticization effect in starch (Reddy & Yang, 2010) resulting in more flexibility morphology of starch resulting in increased mobility factor.

4. Temperature dependence of conductance

Fig. 3(a) shows the temperature dependence of ionic conductivity. The conductivity of starch based polymer electrolyte has shown a slight increase with temperature in the range from 20 to 70 °C. Above 70 °C starch starts burning hence restricted the experiment. The linear variation of plot is analysed by considering Arrhenius type of behaviour. Table 1 shows the values of the different parameters such as A, n and range of ω at different temperatures.

The calculated values of mobile ion concentration (K) and mobility factor (μ_f) are given in Fig. 3(b). Starch is a water absorbing material and it contains a good amount of water in the matrix. There are two types of water present in potato starch one loosely bond and other one tightly bond (Tang, Godward, & Hills, 2000). Hence on heating starch based material, water available in the channel (i.e. loosely bond water) will come out of the matrix very easily. Water itself behaves as charge carrier; hence decrease in water content will result in decreased number of mobile ion which is reflected in decrease in K at nearly ~50 °C as shown in Fig. 3(b). We expect two phenomenon competing with each other (i) increased number of charge carriers due to effect of temperature on dissociation of NH_4I and (ii) decreased number of charge carriers due to decreasing amount of water molecules in the system. The behaviour of μ_f with temperature can be understood on the same line. Since, increase

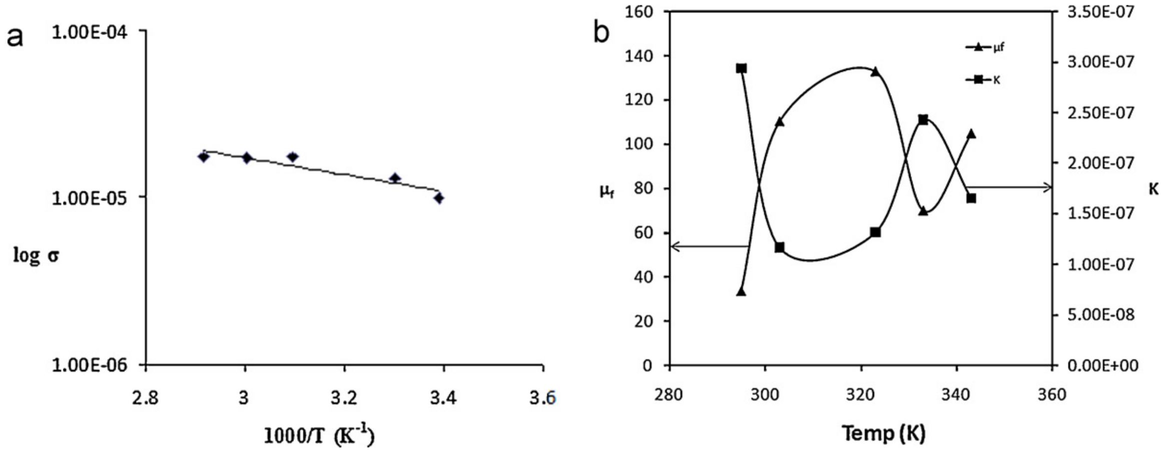

Fig. 3. (a) Variation of conductivity with temperature, (b) variation of carrier ion concentration (K) and mobility factor (μ_f) with temperature.

in mobile ion concentration will augment the chance of collision which will decrease μ_f. Hence μ_f and K are showing inverse trend.

4.1. Frequency dependent conductivity

Conductivity formalism is an excellent tool to have an insight of ion conduction mechanism. For a long time "Universal Power Law"/"Universal Dielectric Response" [UPL/UDR] proposed by Jonscher (1977) has been considered as a thumb rule to understand ion dynamics. The law can be described in mathematical form as:

$$\sigma = \sigma_0 + A\omega^n$$

where, σ = ac conductivity, σ_0 = dc conductivity, A = pre exponent factor and n = power law exponent. The law says that value of exponent (n) in $\sigma = \sigma_0 + A\omega^n$ can be $0 < n < 1$ (Ramesh & Arof, 2001). For good ion conductors, n is supposed to be $\simeq 0.5$. Value of $n \simeq 1$ is explained as long range hopping comparable to sample dynamics and values less than that is explained as increasing tortuous path for ion conduction. Recently, values $n > 1$ has been reported in literature and many new theories have been developed (Funke, Banhatti, & Cramer, 2005; Ke, Huang, Yu, & Zhou, 2010; Pas, Banhatti, & Funke, 2006) explaining the origin of $n > 1$ and predicted that n can have values $0 < n < 2$. The beautiful relationship of time–temperature overlap, in such curves, has been explained by these theories. Theory emphasize that value of n will depend upon frequency and temperature range under consideration. A typical Log σ vs. Log ω ($\sigma = \sigma_0 + A\omega^n$) curve consists of portions with different slopes starting from lower frequency $n \simeq 0$ (dc conductivity); $n \simeq 0.5$ (ion conduction governed by translation motion); $n \simeq 1$ (NCL – Nearly Constant Loss a phenomenon governed by displacive movement of caged ions); $n > 1$ covers other ion movements such as vibrational etc. (Funke, Singh, & Banhatti, 2007). Recently, MIGRATION concept (Mismatch Generated Relaxation for the Accommodation and Transport of ION) (Pas et al., 2006; Funke et al., 2005) is given to explain the phenomenon in polymer electrolytes. Theories predict that values $n \simeq 1$ will be found in GHz range and at low temperature. Popularity of UDR in earlier time can be correlated with limited data (in Hz to KHz/MHz range) availability in that era. Fig. 4 shows the Log σ vs. Log ω curve for the present system at different salt concentration. Log σ vs. Log ω curve for highest conducting salt is inserted in Fig. 4 separately for analysis named (a). The plot consists of three regions, indicated by three straight lines on the curve. The temperature range is very small, which could not be extended because starch burns above 70 °C, hence a well defined conclusion cannot be achieved. But the available data indicates, decreasing n with increasing temperature (if

Table 1
Variation of power law exponent and pre-exponent factor with temperature for different region of frequency.

Temperature (K)	A	n
Higher frequency		
295	$6.89 \times 10–^{13}$	1.21
303	4.20×10^{-12}	1.10
323	6.22×10^{-11}	0.93
333	2.72×10^{-11}	0.98
343	2.96×10^{-11}	0.98
Mid frequency		
295	2.77×10^{-8}	0.53
303	4.53×10^{-8}	0.49
323	9.25×10^{-8}	0.45
333	4.47×10^{-8}	0.50
343	5.36×10^{-8}	0.49
Lower frequency		
295	1.01×10^{-6}	0.22
303	6.20×10^{-6}	0.08
323	5.62×10^{-6}	0.10
333	3.35×10^{-6}	0.13
343	2.10×10^{-6}	0.16

Pre-exponential factor and power law exponent with temperature for different region of frequencies.

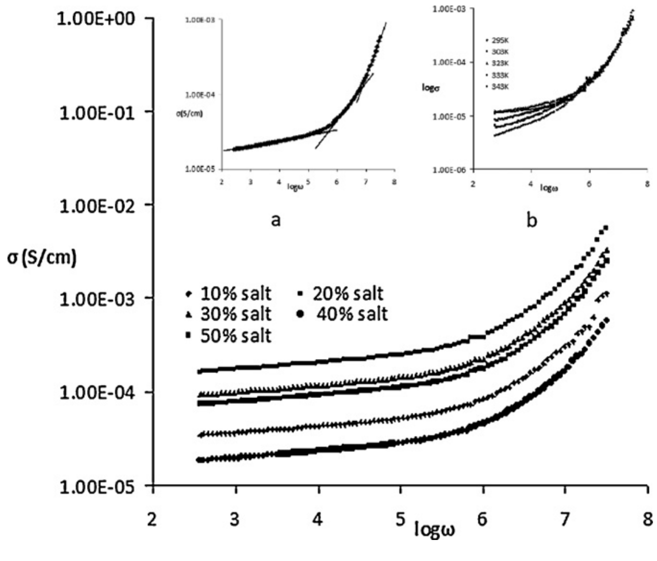

Fig. 4. Frequency dependence of conductivity at different salt concentration, inset (a) variation of Log σ vs Log ω with temperature, inset (b) fitting for three different phenomenon.

same frequency range is selected for NCL fitting). This indicates that on heating caged ions are getting free hence more fraction of ions are shifting to translational motion from displacive/vibrational motion. We should keep in mind that at no stage all ions will perform displacive movement or translation motion (Funke et al., 2007), instead it is a statistical phenomenon and both the processes co-exist. This coexistence of many transport phenomenon simultaneously results in little bit different values of n instead of exactly 0, 1 or 2 as predicted by theories. Inset (b) in Fig. 4 shows the Log σ vs. Log ω curve at different temperatures. At low frequency, curves are clearly separated but they merge at higher frequency. NCL to ion hopping crossover frequency changes with temperature. This is a typical behaviour of NCL phenomenon (Funke et al., 2002). If the NCL fitting parameters are calculated after ion hopping to NCL crossover frequency fitting parameters for all the curves are same ($A \simeq 3.14 \times 10^{-11}$ and $n \simeq 0.98$).

4.2. Dielectric relaxation study

Dielectric formulism is useful in revealing many particulars about conductivity behaviour of any material. The dielectric constant is a measure of stored charge. The frequency dependence of real (ε')and imaginary (ε'') part of the dielectric constants are shown in Fig. 5(a) and (b). The variation of ε' and ε'' with temperature has been shown as insets in Fig. 5(a) and (b) respectively. ε' and ε'' are calculated by using the following relation:

$$\varepsilon' = \frac{(-Z''/Z'2+Z''^2)\times 1}{\omega C} \text{ and } \varepsilon'' = \frac{(-Z'/Z'^2+Z''^2)\times 1}{\omega C}$$

where Z' and Z'' are the real and imaginary part of the impedance, ω is the angular frequency and C is the capacitance of empty measuring cell of electrode area A and sample dimension L.

$$C = \frac{\varepsilon_0 A}{L}$$

At low frequency high values of ε' and ε'' regions are caused by electrode polarisation (Mishra & Rao, 1998). At high frequency, the periodic reversal of the electric field is so fast that ion diffusion in electric field is not feasible. Hence charge accumulation at electrode decreases leading to decrease in ε' and ε'' (Vieira, Avellaneda, & Pawlicka, 2007).

4.3. Modulus formalism

The abrupt increase in ε' and ε'' values at lower frequency side is due to large contribution of electrode polarisation effect. Hence ionic conduction relaxation is misjudged in dielectric formulism. Modulus formalism is discovered to overcome this problem and is widely used to analyse the different relaxation phenomenon in the polymeric system. The ε^* data can be transformed in to M^* formalism by equations given below:

$$M^* = \frac{1}{\varepsilon^*} = M' + iM'' = \left\{\frac{\varepsilon'}{\varepsilon'^2+\varepsilon''^2}\right\} + \left\{\frac{\varepsilon''}{\varepsilon'^2+\varepsilon''^2}\right\}$$

where M' and M'' are the real and imaginary parts of electrical modulus.

Fig. 6(a) and (b) shows the M' and M'' as a function of Log ω for different salt concentration. Peaks at a very high frequency are invariably present in all the complexes and height of the peaks changes with salt concentration. This indicates a relaxation phenomenon is occurring (Mishra, Baskaran, Ramakrishnan, & Rao, 1998) with a relaxation time ~6.64×10^{-8} s.

The curves of M' and M'' vs. frequency, at various temperatures, are shown as inset in Fig. 6(a) and (b) respectively. The M' shows a increasing trend with frequency where as peaks are observed in the M'' spectra in the higher frequency region. The peak in modulus formalism confirms ionic conduction in the system (Ramesh & Arof, 2001). Peak, in modulus formalism, shifts with temperature. But in present case this variation is not very clear. It may be because of two reasons (i) temperature range is not wide enough and (ii) conductivity does not vary too much with temperature and hence shift in modulus peak is not very appreciable.

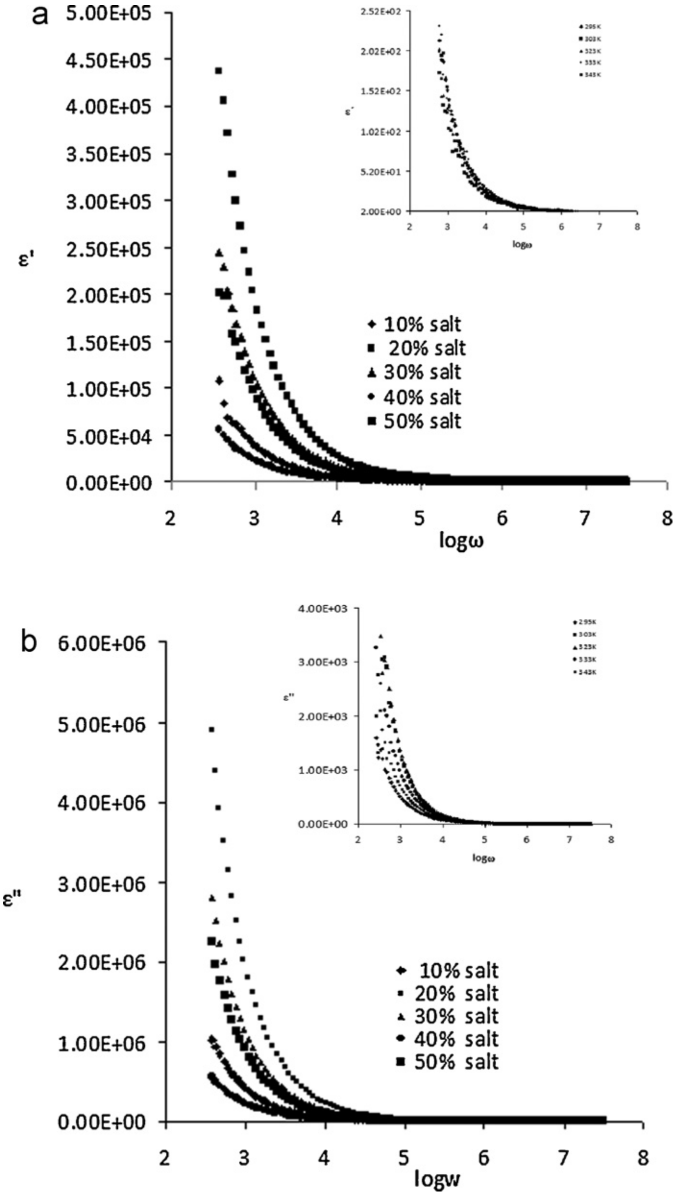

Fig. 5. (a) Variation of dielectric constant with wt% of salt, (b) variation of dielectric loss with wt% of salt.

5. Humidity dependence of conductivity

The effect of humidity on the sample (i.e. from 20% to 99%) has been investigated at room temperature. The experimental set-up used for the measurement is discussed elsewhere (Tiwari, Pandey, et al., 2011; Tiwari, Srivastava, et al., 2011). For data presentation impedance is preferred over conductivity because area and thickness of the material changes when it absorbs/desorbs water, also impedance/conductance are more important parameters than the resistivity/conductivity for device fabrication. Fig. 7 shows the variation of normalized weight increase and impedance with relative humidity (RH %). It is observed that when starch based

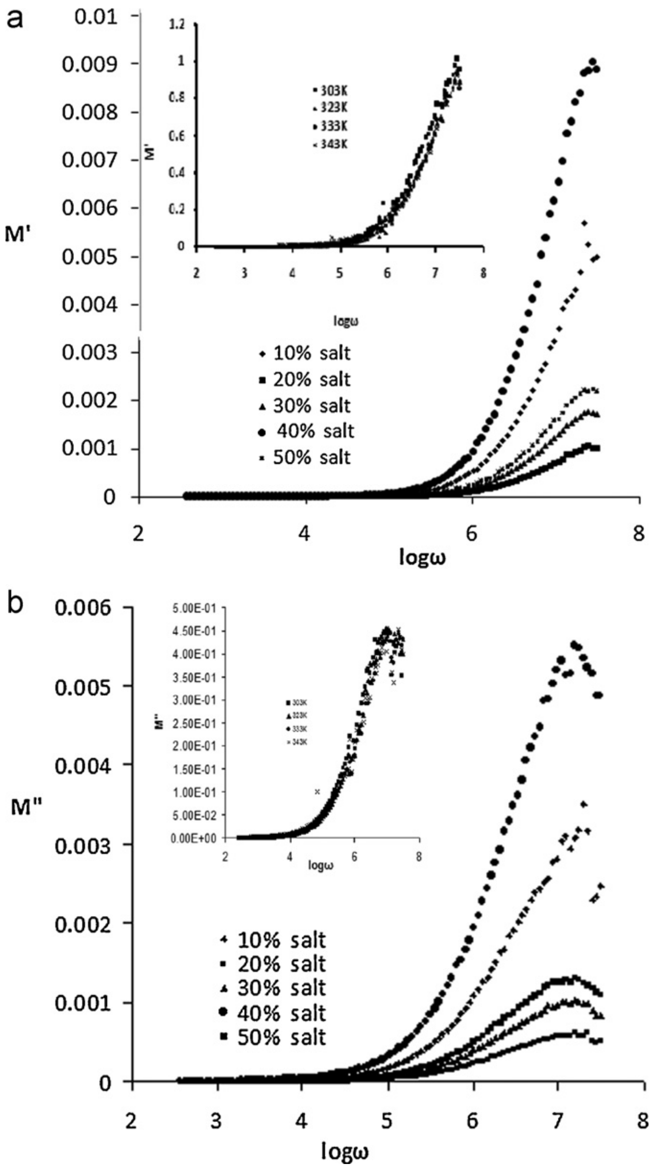

Fig. 6. (a) Variation of M' with wt% of salt, (b) variation of M'' with wt% of salt.

electrolyte was exposed to humid condition the material gains mass due to hydrophilic nature, leading to reduced stiffness. Humidity is expected to have two fold effects; one is providing a channel for ion movement and other one is to increase the number of charge carriers by assisting salt dissociation and by its own dissociation. Conductivity remains nearly constant up to RH ~ 75%, which makes such materials immune to atmospheric changes. Potato starch holds water molecules in two states; one is tightly bond and the other one is loosely bond. Ambient immunity is reported for potato starch + NaI system also (Tiwari, Pandey, et al., 2011; Tiwari, Srivastava, et al., 2011). The ambient immune nature of conductivity in these systems is explained by the fact that water molecules are liberated during the cross-linking of GA and starch. These liberated water molecules (Tahlawy, Venditti, & Pawlak, et al., 2007), are expected to be present in the system as strongly bounded molecules. These are not affected by humidity changes hence conductivity is not affective too much up to this level. Whereas at high humidity levels (i.e. at high water vapour pressure), some water molecules may slip in the channels which will be loosely bound molecules and are free to take part in the conductivity (Olszewska, 2003; Argun et al., 2010) hence conductivity changes with humidity change.

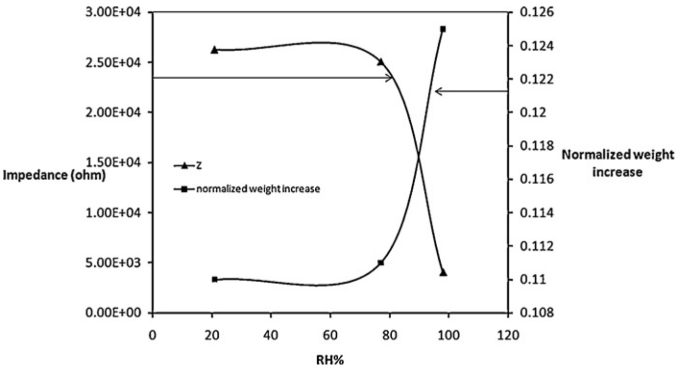

Fig. 7. Variation of impedance and normalized weight increase with relative humidity.

6. Conclusion

The starch based biodegradable polymer electrolyte has been prepared by standard solution cast technique. Ionic conductivity ~2.40×10^{-4} S/cm and ionic transference number ≥ 0.95 indicates that prepared film is ionically conducting. Parameters such as ion concentration factor (K) and mobility factor (μ_f) have been studied with temperature and salt concentration. Ion dissociation factor (n/n_0) has also been studied to get a correlation with K. Relation between the conductivity trend, mobile ion concentration factor (K) and mobility factor (μ_f) with respect to salt concentration and temperature, is established. In conductivity formalism, different regions such as i.e. σ_{dc} at lower frequency, NCL region at mid frequency and superlinear at higher frequency have been discussed. All the fitting parameters have been calculated. $n \sim 1$ confirms the NCL region governed by displacive movement of caged ions. In starch based electrolytes NCL is occurring at much lower frequency and higher temperature in comparison to theoretical predictions. At low frequency, the variation of dielectric constant with frequency suggests electrode interface polarisation process. At low frequency the high value of dielectric constant and loss is due to electrode polarisation. Material is humidity immune up to 77% RH and a very small variation with temperature has been found hence results are encouraging for possible use of starch based electrolytes in humidity immune devices.

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