RESEARCH ARTICLE OPEN ACCESS

Preparation and Characterization of Lithium Ion Conducting Solid Polymer Electrolytes from Biodegradable Polymers Starch And PVA

B. Chatterjee, N. Kulshrestha and P.N. Gupta
Department of Physics, Banaras Hindu University, Varanasi, UP 221005, India
Corresponding author Postal address: Department of Physics, Banaras Hindu University, Varanasi, UP 221005, India.

Abstract

Solid Polymer electrolyte films have been prepared from Starch-Poly vinyl alcohol (PVA) blend a well acknowledged biodegradable material. Solution cast technique was employed for the preparation of solid polymer electrolyte films added with Lithium Bromide (LiBr) salt. X-ray diffraction (XRD) studies of the prepared films portrayed the evolution of an amorphous structure with increasing content of salt which is an important factor that leads to the augmentation of conductivity. Electrochemical impedance spectroscopic analysis revealed noticeable ionic conductivity ~ 5x 10^{-3} S/cm for 20 wt% of salt at ambient conditions. Ionic conductivity showed an increasing trend with salt content at ambient conditions. Transference number measurements confirmed the ionic nature of the prepared solid polymer electrolyte films. Dielectric studies revealed a sharp increase in the number of charge carriers which contributed to enhancement in conductivity. Low values of activation energy extracted from temperature dependent conductivity measurements could be favorable for device applications. For the composition with highest conductivity a temperature independent relaxation mechanism was confirmed by electric modulus scaling.

Key words: Solid Polymer electrolytes, XRD, Ionic Conductivity, Dielectric Properties.

I. Introduction

The study of Poly ethylene Oxide (PEO) complexed with Sodium and Potassium Thiocynates by Wright *et al* marked the genesis of a new class of materials known as the Solid polymer electrolytes (SPEs) [1]. SPEs synergize the flexibility, mould ability and mechanical strength of the solid state with the ionic conductivity of the liquid state which makes them promising candidates for application in compact and light weight electrochemical devices of the modern age. However realization of appreciable ionic conductivity at ambient conditions in SPEs still remains a challenge. In course of time a large number of polymer salt complexes have been studied with the objective to achieve ionic conductivity comparable to the liquid electrolytes. Recently, increasing concern for environmental safety has turned the interest of researchers towards natural (cellulose, Chitosan, Starch, etc) polymers for preparing solid polymer electrolyte films. Apart from being safe to the environment these bio films or bio plastics provide suitable electrode/electrolyte contact and posses mechanically adhesive qualities which promote their use in ionic conductors [2, 3]. Starch is a natural polymer abundantly found in almost every corner of the globe. The most common sources of Starch include corn, wheat, rice, potato, cassava etc. The basic architecture of Starch comprises of two polymers Amylose and Amylopectin. Amylose molecules consist of 200–20,000 glucose units which form a helix as a result of the bond angles between the constituent glucose units. Amylopectin is a highly branched polymer containing short side chains of 30 glucose units attached to every 20–30 glucose units along the chain. [4].Ratio of Amylose and Amylopectin is one of pivotal factors which decide the properties of Starch based films. Concurrent literature shows a noticeable number of reports on Starch based polymer electrolytes [5-20]. The reported ionic conductivity values at ambient conditions lie in the range 10^{-5} to 10^{-4} S/cm. Recently Ramesh *et al* [14] reported ionic conductivity ~10^{-3} S/cm in corn Starch based SPE with deep eutectic solvent as an additive. Realization of considerable ionic conductivity in Starch based films requires suppression of crystalline phases of Starch to the maximum extent. Crystallinity in Starch can be reduced by incorporating plasticizers like glycerol and water. Nevertheless at higher contents of plasticizer the mechanical properties of the film are compromised. Certain flaws like large water absorption, brittleness, and low mechanical strength restrict the widespread application of pure Starch films. Blending Starch with synthetic or natural biodegradable polymers has been established as an effective remedy of these problems [4]. PVA is a water soluble, cost effective biodegradable synthetic polymer with excellent film forming capacity. The miscibility of Starch and PVA is promoted by the formation of hydrogen bonds [4]. Blending of Starch with PVA is effective in overcoming retrogradation which is a common problem in Starch based systems [21]. Starch-PVA blend films with improved mechanical strength have been acknowledged as potential materials for applications in many spheres of industry. In the present paper Starch-PVA blend has been investigated as a new material for biodegradable solid polymer electrolytes. Electrical properties of Starch (60wt %) PVA (40wt %) blend added with Lithium Bromide (LiBr) in different weight ratios have been studied. Structural changes occurring in the polymer matrix with the addition of salt have been investigated and correlated with the observed electrical properties.

II. Materials and Methods

2.1 *Materials and Preparation of polymer electrolyte films*

Starch Soluble (Himeedia Pvt Limited India, Botanical source Potato), Polyvinyl Alcohol (Mw. 125,000), Lithium Bromide (S.D. Fine Chemicals Boisar Mumbai India), Glycerol (Qualigen Fine Chemicals India) and Glutaraldehyde (Merck India) were used for the preparation of solid polymer electrolytes by solution casting method [19]. In Starch-PVA blends a vital role is played by crosslinkers and plasticizers. Plasticizers reduce the brittleness and glass transition temperature of Starch based films which are fundamental requirements for attaining higher conductivity. Glycerol has been acknowledged as a versatile plasticizer in Starch based films. Crosslinkers serve to render mechanical strength to the films. A recent study made by Tiwari et al [10] has established that Glutaraldehyde is not only an effective crosslinker but also improves conductivity in Starch based films.

Starch and PVA in 60:40 ratio by weight were dissolved in 150 ml triply distilled water at 90^0C using magnetic stirring. After stirring for about 2 hours Glutaraldehyde and glycerol were added to the viscous solution. Glutaraldehyde and glycerol in 60:40 ratio to each other constituted 30 wt% of the total weight of the sample. LiBr salt in 5, 10, 15 and 20wt% were added to the viscous solution. The final solution was poured in propylene petri dishes and left at room temperature for solvent evaporation. The composition and coding of the prepared films are as follows (i) **0%LiBr--------L-0** (ii) **5%LiBr--------L-5** (iii) **10%LiBr-------L-10 (iv) 15%LiBr--------L-15 (v) 20%LiBr--------L-20.**

III. Characterization

3.1. X-Ray diffraction

X-ray diffraction patterns of the Starch-PVA polymer electrolyte films with different contents of LiBr were recorded in 2θ range 15 to 40^0 at room temperature from an XPERT-PRO diffracto meter. The system was operated at 40 kV, 30mA. Step size of measurement was fixed at $2\Theta=0.02^0$ at a scan speed of 0.5s/step. To avoid retro gradation of Starch the XRD measurements were carried out within an hour after the film preparation. [22]

3.2. AC Conductivity.

Films of average thickness ˜ 500μm were chosen for electrical measurements. The cell structure for the electrical measurements can be described as Al│Starch-PVA blend electrolyte│Al [23]. Impedance data were recorded by sandwiching the films between two similar brass electrodes. For making good electrical contacts polymer electrolyte films cut in circular shape were covered with Aluminum foil on both sides.HIOKI-3532 LCR Bridge operating in the frequency range 42Hz -5MHz was used to record the electrochemical impedance data. Temperature dependent Impedance data was recorded by placing the sample holder in temperature controlled furnace with an accuracy of 5^0C.

3.3 Bulk Conductivity

Bulk conductivity of the polymer electrolyte films at different temperatures and salt contents was calculated using expression 5 where *l* is the thickness and A is the area of cross section of the polymer electrolyte film. Bulk resistance R_b was obtained from the intercept of the Nyquist plot on the Z' axis.

$$\sigma_{dc}=\frac{1}{R_b}\left(\frac{l}{A}\right) \text{------------------------------------}(1).$$

3.4. Dielectric Studies

The dielectric parameters ϵ' and ϵ" were calculated from the impedance data using the expressions 6 and 7 [17]

$$\varepsilon' = \left(\frac{1}{\omega C_0}\right)\left(\frac{Z''}{Z'^2+Z''^2}\right) \text{—} (2)$$

$$\varepsilon'' = \left(\frac{1}{\omega C_0}\right)\left(\frac{Z'}{Z'^2+Z''^2}\right) \text{– —} (3)$$

Where Z′ and Z″ are the real and imaginary parts of impedance, ω= 2πf, f is the frequency in Hz and C_0 is the free space capacitance obtained from the expression (8)

$$C_0=\varepsilon_0\left(A/d\right) \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_}(4)$$

Where *A* is the electrode-electrolyte contact area and *d* is the thickness of the polymer electrolyte film, ε_0 is the permittivity of free space.

3.5. Transference Number

Transport properties of the Starch-PVA polymer electrolyte films were studied by Wagner's Polarization technique [10]. A dc voltage of 0.5 volts was applied across the electrodes and the current (μA) was measured against time (seconds).Transference numbers were obtained from the expression

$$t_{ion} = \frac{I_{initial} - I_{final}}{I_{initial}} \qquad (5)$$

Where, I $_{initial}$ is the current due to ions and electrons I $_{final}$ is the current due to electrons.

3.6.Electric Modulus Studies

The real and imaginary parts of the complex modulus are defined in terms of the dielectric constant and dielectric loss by the following relations [26]

$$M' = \frac{\varepsilon'^2}{\varepsilon'^2 + \varepsilon''^2} \qquad (6)$$

And

$$M'' = \frac{\varepsilon''^2}{\varepsilon'^2 + \varepsilon''^2} \qquad (7)$$

IV. Results and Discussion

4.1. X-ray diffraction studies.

Figure 1shows the X-ray diffraction patterns of the Starch-PVA blend polymer electrolytes with different contents of LiBr in the 2Θ range 15 to 40^0 at room temperature. The presence of peaks at 17^0, 22^0, 24^0 and 26^0 in the X- ray diffraction pattern of the sample L-0 provides ample evidence of the *B* polymorph of Starch [22, 27, 29]. In case of Starch-PVA blends the peak at 19^0 results from the crystalline contribution of PVA [28]. From the XRD patterns it is clearly observable that the noticeable peaks in the XRD pattern of the film L-0 gradually become imperceptible with increasing salt content. The XRD pattern of the sample with highest conductivity L-20 is devoid of any distinct peak which is a reflection of highly amorphous structure [30]. The central feature exhibited by the XRD patterns of the polymer electrolyte films is the suppression of the crystalline phases due to Starch and PVA which results in the increase of conductivity with salt content [31]. The absence of peaks corresponding to LiBr affirms the complete dissolution of the salt in the polymer matrix [32-35]. The XRD profile of the sample L-20 is almost devoid of any peak corresponding to Starch or PVA and exhibits the feature of a highly amorphous system. The evolution of a highly amorphous structure in this sample may be attributed as a key factor that brings a large enhancement in ionic conductivity.

4.2. Frequency Dependent conductivity

AC conductivity spectrum reflects the synergistic effect of migration of charge carriers at low frequencies and dispersion at higher frequencies [36]. Figure 2(a) shows the ac conductivity of the Starch-PVA polymer blend electrolyte films with different contents of LiBr at room temperature. From figure 2 it is evident that for all the samples ac conductivity increases with salt concentration. The enhancement of the ac conductivity with increasing salt concentration can be attributed to the increase in the number of mobile charge carriers and to the tremendous increase in the ionic mobility occurring due to the absorption of energy from the ac signal. The increase in conductivity with frequency is a signature of hopping mechanism prevalent in the polymer electrolyte systems [36, 37].Low frequency dispersions observed in the samples L-5 and L-10 are attributed to electrode polarization effects [38]. From figure 2 it can be observed that the frequency independent plateau region is almost absent in all the polymer electrolyte samples. The absence of the plateau region in the ac conductivity spectra is attributed to the dominance of capacitance admittance over the resistors [39]. These types of effects are quiet expected in systems like Starch where the presence of traps, pores and other forms of structural in homogeneities are inherent [38,40 41]. Figure 2 (b) shows the ac conductivity at different temperatures for the film L-20. It could be observed from figure 2(b) that at low frequencies and higher temperatures the ac conductivity tends to merge which is the result of dc conductivity [42]

4.3. Concentration dependent conductivity

Figure 3(a) shows the variation of ionic conductivity for the Starch-PVA polymer electrolytes with different contents of LiBr at room temperature. Bulk conductivity of the Starch-PVA blend polymer electrolytes at room temperature was obtained using expression 5. The variation of the conductivity with salt concentration is the outcome of specific interactions between the salt and the polymer matrix [7]. Figure 3(b) portrays the variation dielectric constant with salt content at three different frequencies at room temperature. It can be observed that the variation of dielectric constant with salt content follows almost the same trend as ionic conductivity [7].In case of polymer electrolytes the amorphicity of the polymer matrix and the increase in the number of charge carriers are the major factors that contribute in increasing the ionic conductivity. In the present system the increase in amorphicity due to the suppression of the crystalline phases is corroborated by the XRD studies. Increase in the dielectric constant with salt content affirms the amplification in the number of charge carriers. Thus, the collaborative effect of amorphicity and increase in the number of charge carriers results in the realization of maximum conductivity 5x 10^{-3} S/cm in the sample L-20.The continuous increase in conductivity with salt content is a strong evidence that corroborates the transport of ions through hopping [44]. The analysis of the bulk conductivity studies asserts that the highly amorphous structure and the ability to sustain a high degree of salt dissociation establish the worth Starch-PVA blend as a promising material for biodegradable solid polymer electrolytes. The magnitude of ionic conductivity realized in the present system is noticeable compared to several reports on Starch based polymer electrolytes [5-13] which is an aspect of momentous significance. Another noteworthy feature of the salt content vs conductivity profile is the unbroken increase of conductivity with salt content which can be attributed to the solubility of the salt and structural modifications in the polymer matrix [43, 44]

Figure 4 shows the variation of ionic conductivity of the Starch-PVA polymer electrolytes with different contents of LiBr in the temperature range 303K to 373K. The increase in conductivity of the polymer electrolytes with temperature is attributed to the increase in the segmental motion of the polymer matrix. It can be observed from fig 4 that the conductivity of all the samples decrease at around 100^0C which is attributed to the evaporation of water contained in the system. Loss of water results reduces the flexibility of the polymer chains and salt dissociation. In the samples L-5, L-0, L-10 and L-15 the temperature vs conductivity profile shows a sudden jump at a particular temperature. The sudden jump in the conductivity of these three samples is ascribed to the melting of remnant crystalline phases [45]. However no such jump could be observed in the temperature vs conductivity profile of the sample L-20 which is reflects the highly amorphous nature of the sample.

The activation energy for the ionic conduction for the Starch- PVA polymer electrolytes with different contents of LiBr was obtained using the Arrhenius relation

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{KT}\right) \qquad (12)$$

Where σ_0 is the pre exponential factor Ea is the activation energy, K is the Boltzmann constant and T is the absolute temperature. The values of activation energy (E_a) for the polymer electrolyte films with different contents of LiBr are shown in table 1.Lower activation energy values indicate that the Li+ ions require very less energy to overcome the reorganization and re-crystallization process in the polymer system. This aspect is again attributed to the amorphous structure of the polymer matrix [46].Lowest value of activation energy in the L-20 sample shows that the ion movement is facile in this sample [47].

4.4 Dielectric Studies

Figure 5 shows the frequency dependence of the dielectric constant and dielectric loss of the Starch-PVA blend polymer electrolytes with different contents of LiBr at various temperatures. Dielectric constant and dielectric loss show a decreasing trend with increase in frequency. The high values of dielectric constant and dielectric loss observed at low frequencies are attributed to the electrode polarization effect. The frequency independent behavior of the dielectric constant at higher frequencies is attributed to the inability of the dipoles to follow the fast changing electric field or to the decreased number of ions that contribute to polarization [48]. The accumulated charges cause a decrease in the polarization which is manifested as the reduction in the dielectric constant and dielectric loss. The high values of ε' and ε'' at low frequencies are indicative of non Debye behavior.

4.5. Transport properties

The ionic transference numbers of the polymer electrolytes obtained from Wagner's Polarization method were in range **0.90-0.95** which shows that the ions are the dominant charge carriers in the system.

4.6. Electric Modulus Studies

Interfacial Polarization or Maxwell-Wagner–Sillers effect is a common phenomenon observed in the heterogeneous systems like polymer salt complexes, polymer nano composites etc. The difference in the conductivities of the constituent components of the system causes the space charge to build up at macroscopic interfaces [26]. In these systems the conductive components obscure the interfacial relaxation that causes the dielectric constant to be very high at low frequencies. To overcome this difficulty in the study of interfacial polarization, the concept of "*electric modulus*" was introduced. The advantage of electric modulus formalism is that the variations due to large conductivity and permittivity values at low frequencies are minimized in the interpretations of the bulk relaxation properties. **Figure 6** depicts the electric modulus studies Starch-PVA blend polymer electrolytes with different contents of LiBr. Negligible electrode polarization in the films is manifested by the negligible values of M' and M'' at low frequencies. On the other hand the increase of M' with frequency indicates that there are no restoring forces to govern the mobility of the ions which is also suggestive of the long range mobility of the charge carriers [41**]**.The reduction in the M' values with increasing temperature as observed in figure 7 (b) is an indicative of the increased mobility of the polymer segments [41]. The long tail in the M'' spectra on the other hand reflect the large capacitance associated with the electrodes. Additionally the long tail in the M" spectra also provides evidence of the long range ionic hopping predominant in the polymer electrolyte material [50]. The small values associated with M" signify the large capacitance that results in the meager contribution of the electrode polarization effects. Figure 7 (b) shows the temperature dependence of M' and M" of the highest conducting sample L-20 at 1 KHz, 10KHz, 100KHz and 1 MHz. The decrease in the values of both M' and M" confirms that the system is an ionic conductor. Scaling of electric modulus is an effective method in extracting valuable information about the dependence of relaxation dynamics on factors like temperature and composition. Figure 7 (c) shows the scaling behavior of the imaginary part of electric modulus M" at various temperatures for the sample L-20. The merging of the modulus spectra at different temperatures on a single curve signifies that the relaxation mechanism is independent of temperature. The asymmetric shape of the scaled M "reflects the non Debye behavior and the asymmetric distribution of relaxation times [25].

V. Conclusion

In conclusion a versatile biodegradable polymer blend composed of Starch and PVA has been investigated in terms of electrical and structural properties as a new solid polymer electrolyte material. Incorporation of salt in Starch-PVA polymer blend causes the evolution of a highly amorphous structure. Frequency dependent conductivity shows an increasing trend with temperature and salt content. Power law analysis reveals the prevalence of CBH mechanism in the sample showing highest conductivity at room temperature. Low values of activation energy obtained from Arrhenius formalism encourage application in electrochemical devices. Values of M' and M" close to zero revealed by electric modulus investigation confirms the absence of electrode polarization effects. The appreciable value of conductivity obtained at ambient condition implies Starch-PVA blend as a hopeful material for biodegradable solid polymer electrolytes of the future. The results obtained in the present investigation are expected to foster further work on Starch-PVA based solid polymer electrolytes.

Acknowledgement

One of the authors (Bhaskar Chatterjee) is greatly thankful to UGC for providing RFSMS fellowship.

References:

[1] Armand, M. The History of polymer electrolytes, Solid State Ionics , 1994: 69: 309-319

[2] Ma, X., Yu,J, Kang, H., and Wang, N.The Effects of Different Plasticizers on the Properties of Thermoplastic Starch as Solid Polymer Electrolytes. *Macromol Mater Eng*, 2007:292: 503–510

[3] Arrieta A A, Gañán P F, Márquez S E and Zuluaga, R. Electrically Conductive Bioplastics from Cassava Starch. *J. Braz. Chem. Soc*, 2011: 22: 1170-1176.

[4] Tang X and Alavi S. Recent advances in Starch, polyvinyl alcohol based polymer blends nanocomposites and their biodegradability. *Carbohydr. Polym*, 2011: 85: 7–16.

[5] Sudhakar Y.N. and Selvakumar M. Lithium perchlorate doped plasticized chitosan and Starch blend as biodegradable polymer electrolyte for supercapacitors *Electrochim. Acta*, 2012; 78: 398– 405

[6] Majid S.R. and Arof A K. Electrical behavior of proton-conducting chitosan-phosphoric acid-based electrolytes, *Physica B* 2007; 390: 209–215

[7] Khiar A S A and Arof A K. Electrical Properties of Starch/Chitosan-Nh4NO3Polymer Electrolyte, *WASET* 2011; 5: 11-25

[8] Tiwari T, Kumar M, Srivastava N and Srivastava PC. Electrical transport study of potato Starch-based electrolyte system-II. *Mater. Sci. Eng., B* 182; 2014: 6– 13

[9] Yusof Y M, Shukur M F, Illias H A and Kadir M F Z. Conductivity and electrical properties of corn Starch–chitosan blend biopolymer electrolyte incorporated with ammonium iodide *Phys. Scr*. 2014; 89: 035701 (10pp)

[10] Tiwari T, Pandey K, Srivastava N and Srivastava P C. Effect of Glutaraldehyde on Electrical Properties of Arrowroot Starch1NaI Electrolyte System, *J. Appl. Polym. Sci*. , 2011; 121: 1–7

[11] Khanmirzaei M H and Ramesh S. Ionic Transport and FTIR Properties of Lithium Iodide Doped Biodegradable Rice Starch Based Polymer Electrolytes, *Int. J. Electrochem. Sci*., 2013;8: 9977 – 9991

[12] Ning W, Xingxiang Z, Haihui L and Jianping W. N, N-dimethylacetamide/lithium chloride plasticized Starch as solid biopolymer electrolyte, *Carbohydr. Polym*. 2009; 77 : 607–611

[13] Ning W, Xingxiang Z, Haihui Liu and Benqiao H.1-Allyl-3-methylimidazolium chloride plasticized-corn Starch as solid biopolymer electrolytes *Carbohydr. Polym.* 2009; 76 : 482–484

[14] Ramesh S Shanti R and Morris E. Studies on the plasticization efficiency of deep eutectic solvent in suppressing the crystallinity of corn Starch based polymer electrolytes. *Carbohydr. Polym.* 2012; 87 : 701– 706

[15] Shukur M F, Ibrahim F M, Majid N A, Ithnin V and Kadir M F Z. Electrical analysis of amorphous corn Starch-based polymer electrolyte membranes doped with LiI. *Physica Scripta* 2013;88:1-10.

[16] Khanmirzaei M H and Ramesh S. Ionic Transport and FTIR Properties of Lithium Iodide Doped Biodegradable Rice Starch Based Polymer Electrolytes. *Int. J. Electrochem. Sci.* 2013; 8: 9977 – 9991.

[17] Abd El-Kader M F H and Ragab H S. Conductivity and dielectric properties of maize Starch/methylcellulose blend films, *Ionics* 2013;19:361–369

[18] Teoh K H, Ramesh S and Arof A K. Investigation on the effect of nanosilica towards corn Starch–lithium perchlorate-based polymer electrolytes. J. Solid State Electrochem 2012;16:3165–3170

[19] Kumar M, Tiwari T and Srivastava N.. Electrical Transport Behavior of Bio-Polymer Electrolyte System: Potato Starch + Ammonium Iodide", *Carbohydr. Polym*, 2012;88: 54–60.

[20] **Samsudin, Aziz, & Isa,** Ion Conducting Mechanism of Carboxy Methylcellulose Doped With Ionic Dopant Salicylic Acid Based Solid Polymer Electrolytes, International Journal of Applied Science and Technology, **2012;2: 113-121**

[21] Follain N, Joly C Dole and Bliard C. Properties of starch based blends. Part 2. Influence of poly vinyl alcohol addition and photo crosslinking on starch based materials mechanical properties *Carbohydr. Polym*, 2005; 60: 185–192

[22] Bogracheva T Y, Wang Y L, Wang T L and Hedley C. L. Structural Studies of Starches with Different Water Contents. *Biopolymers* 2002;64: 268–281, 2002

[23] Singh K P and Gupta P N. Study of Dielectric Relaxation in Polymer Electrolytes, *Eur. Polym. J.* 1998; 34: 1023-1029.

[24] Khiar A S A and Arof A K Electrical Properties of Starch/Chitosan-Nh4NO3 Polymer Electrolyte. World Academy of Science 2011; 5 : 11-25

[25] Aziz S B and Abidin Z H Z . Electrical Conduction Mechanism in Solid Polymer Electrolytes: New Concepts to Arrhenius Equation, *Journal of Soft Matter* 2013. http://dx.doi.org/10.1155/2013/323868

[26] Tsangaris G M, Psarras G C and Kouloumbi N. Electric modulus and interfacial polarization in composite polymeric systems. *Journal Of Materials Science* 1998;33: :2027-2037

[27] Wang T L Bogracheva T Y and Hedley C L. Starch: as simple as A, B, C? *J. Exp. Bot.* 1998; 49:481–502.

[28] Sreekumar P A, Al-Harthi A M and De S K. Studies on Compatibility of Biodegradable Starch/Polyvinyl Alcohol Blends. *Polym. Eng. Sci.* 2012; 52: 2167-2172

[29] Wang S, Yu J, Zhu Q,Yu J and F Jin. Granular structure and allomorph position in C-type Chinese yam Starch granule revealed by SEM,13C CP/MAS NMR and XRD, *Food Hydrocolloid* 2009;23: 426–433.

[30] Das A, Thakur A K and Kumar K. Exploring low temperature Li ion conducting plastic battery electrolyte *Ionics* 2013;19:1811–1823.

[31] Wu Y, Chen Z, Li X and Li M. Effect of tea polyphones on the retrogradation of rice Starch. *Food Res Int* 2009;42:221–225

[32] Babuand R S and Rani M U. Effect of complexing salts on PVC/PEO Polymer blend Electrolyte *Bull. Mater. Sci.* 2011**;** 34: 1525–1530.

[33] Flora X H, Ulaganathan M and Rajendran M. S. Influence of Lithium Salt Concentration on PAN-PMMA Blend Polymer Electrolytes *Int. J. Electrochem. Sci.* 2012; 7:7451 – 7462.

[34] Singh T J and Bhat S V. Morphology and conductivity studies of a new solid polymer electrolyte: (PEG) x$LiClO_4$ *Bull. Mater. Sci.* 2003;26:707–714

[35] Chandra Sekhar P, Kumar PN, Sasikala U, Rao V VR N and Sharma A.K. Investigations on lithium ion complexed polyvinyl chloride (PVC) solid polymer electrolyte films. *Engineering Science and Technology*, 2012; *2*: 2250-3498.

[36] Hanafy T. A. Dielectric relaxation and alternating current conductivity of lanthanum, gadolinium, and erbium-polyvinyl alcohol doped films *J. Appl. Phys.* 2012; 112: 034102-10.

[37] Dyre J C The random free energy barrier model for ac conductivity in disordered solids, *J. Appl. Phys* 1988; 64, 2456-2468.

[38] Almond D P The extraction of ionic conductivities and hopping rates from a.c. Conductivity data *J. Mater. Sci.* 1984;19:3236-3248,

[39] Dyre J.C. Some remarks on the ac conduction in disordered solid *J. Non-Cryst. Solids*, 1991;135: 219-226.

[40] Papathanassiou A N , Sakellis I and Grammatikakis J. Universal frequency-dependent ac conductivity of conducting polymer networks, *Appl. Phys. Lett.* 2008; 91, 122911 – 122922.

[41] Vishwakarma P.N. AC Conductivity in Boron Doped Amorphous Conducting Carbon Films on the Insulating Side of MI Transition. *J. Appl. Phys*. 2006; 100: 113702-5.

[42] Das P R, Pati B, Sutar B C and Choudhury R N P. Study of Structural and Electrical Properties of a New Type of Complex Tungsten Bronze Electroceramics; $Li_2Pb_2Y_2W_2Ti_4V_4O_{30}$, *Journal of Modern Physics* 2012; 3: 870-880.

[43] Gondaliya N, Kanchan D K, Sharma P and Joge P. Structural and Conductivity Studies of Poly(Ethylene Oxide)—Silver Triflate Polymer Electrolyte System *Materials Sciences and Applications* 2011;l2:1639-1643.

[44] LimYu, J An,Y.H. and Jo N J. Polystyrene-Al2O3composite solid polymer electrolyte for lithium secondary battery *Nanoscale Res. Lett.* 2012;7: 1-6.

[45] Mohapatra S R, Thakur A Kand Choudhary R N P Studies on PEO-based sodium ion conducting composite polymer films *Ionics* 2008; 14: 255–262,

[46] Liew CW, Ramesh S, Ramesh K and Arof A K. Preparation and characterization of lithium ion conducting ionic liquid-based biodegradable corn Starch polymer electrolytes *J. Solid State Electrochem*. 2012; 16:1869–1875

[47] Zainol NH, Samin SM, Othman L, Isa KB M, Chong WG and Osman Z. Magnesium Ion-Based Gel Polymer Electrolytes: Ionic Conduction and Infrared Spectroscopy Studies. *Int. J. Electrochem. Sci* 2013; 8:3602 - 3614

[48] Ali T M, Padmanathan N and Selladurai S. Structural, conductivity, and dielectric characterization of PEO–PEG blend composite polymer electrolyte dispersed with TiO_2 nanoparticles *Ionics* 2013;19:1115–1123.

[49] Mudarra M, Calleja RD, Belana J , Can ˜adas JC, Dieg, JA, Sellare`s J and Sanchis, MJ. Sublinear dispersive conductivity in polymethyl methacrylate at temperatures above the glass transition *Polymer* 2004;45:2737–2742.

[50] Harun N I , Ali R M, Ali A. M. M and Yahya M Z A. Dielectric behaviour of cellulose acetate-based polymer electrolytes *Ionics* 2012;18: 599–606

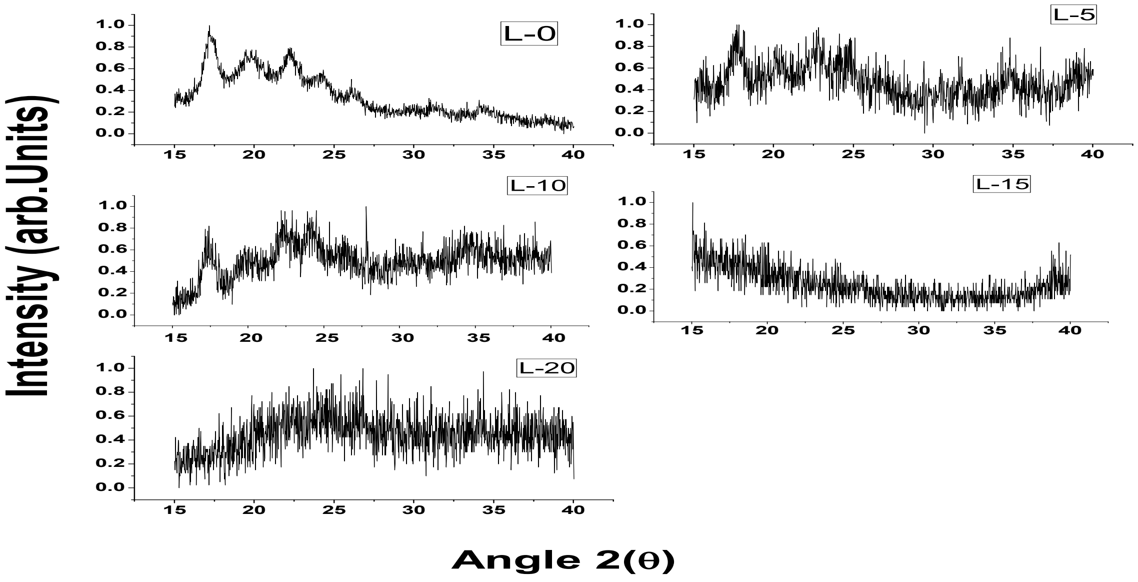


Figure1 X ray Diffraction pattern of Starch-PVA polymer electrolytes with different contents of LiBr.

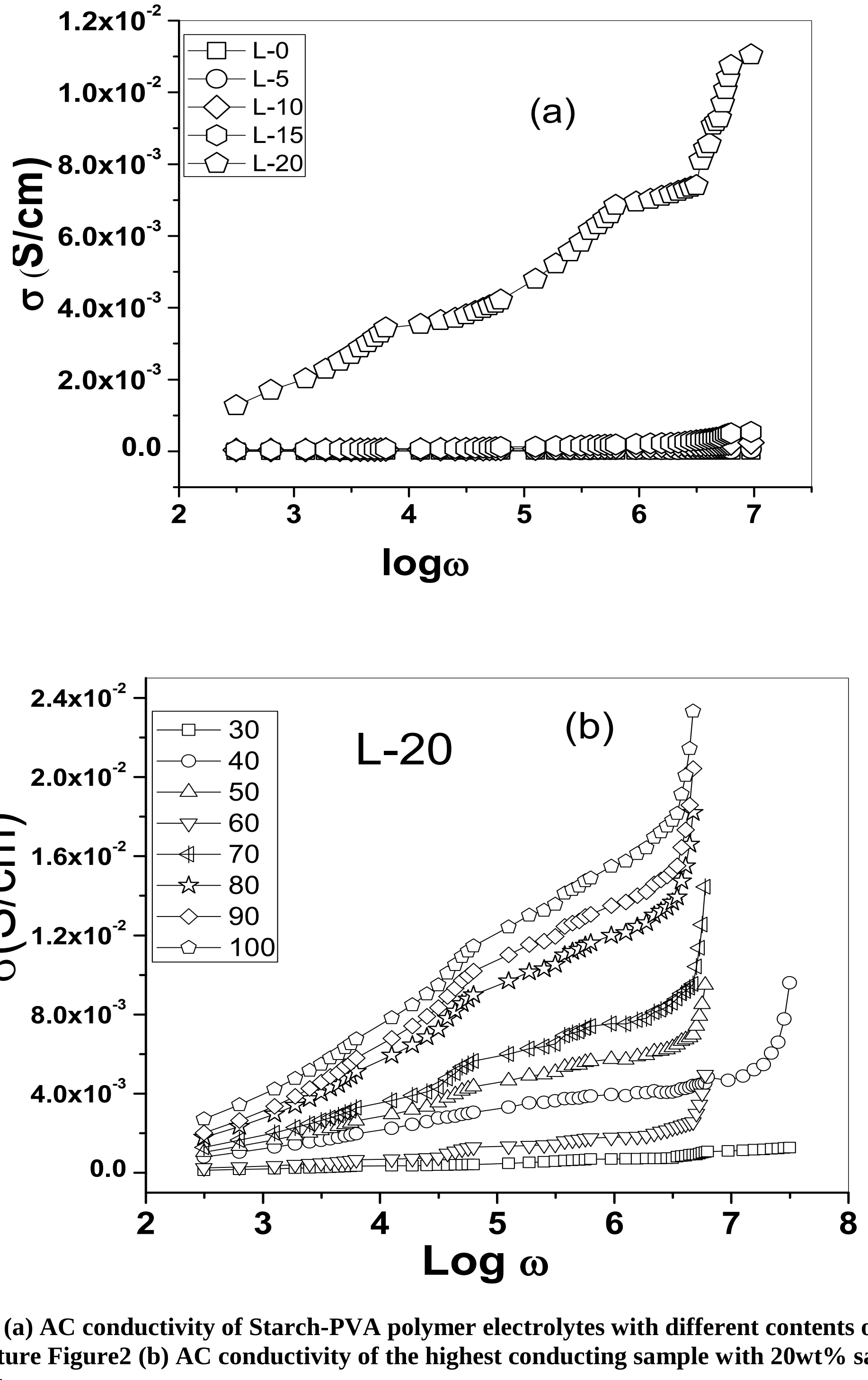


Figure 2 (a) AC conductivity of Starch-PVA polymer electrolytes with different contents of LiBr at room temperature Figure2 (b) AC conductivity of the highest conducting sample with 20wt% salt at different temperatures

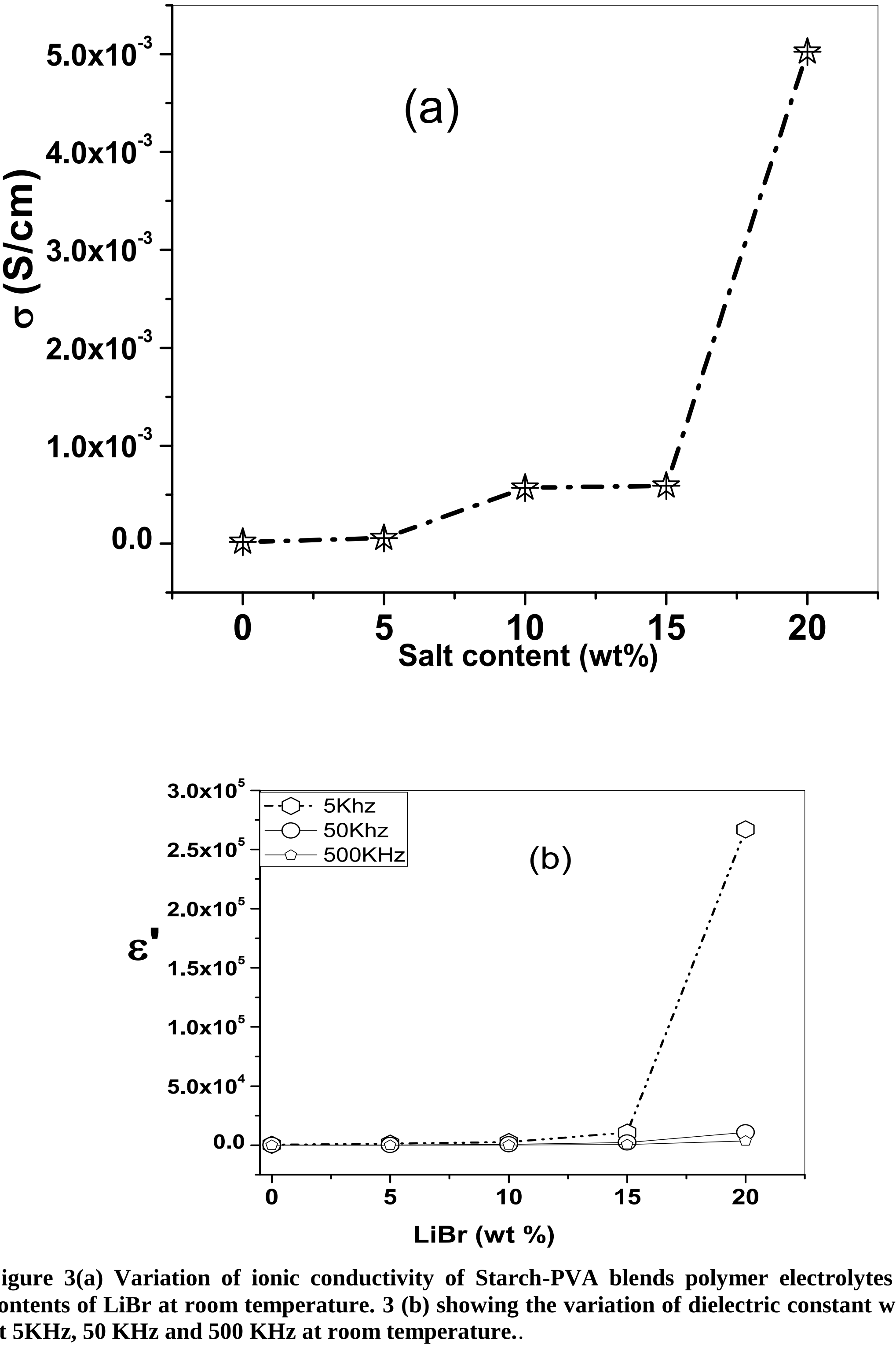


Figure 3(a) Variation of ionic conductivity of Starch-PVA blends polymer electrolytes with different contents of LiBr at room temperature. 3 (b) showing the variation of dielectric constant with salt content at 5KHz, 50 KHz and 500 KHz at room temperature..

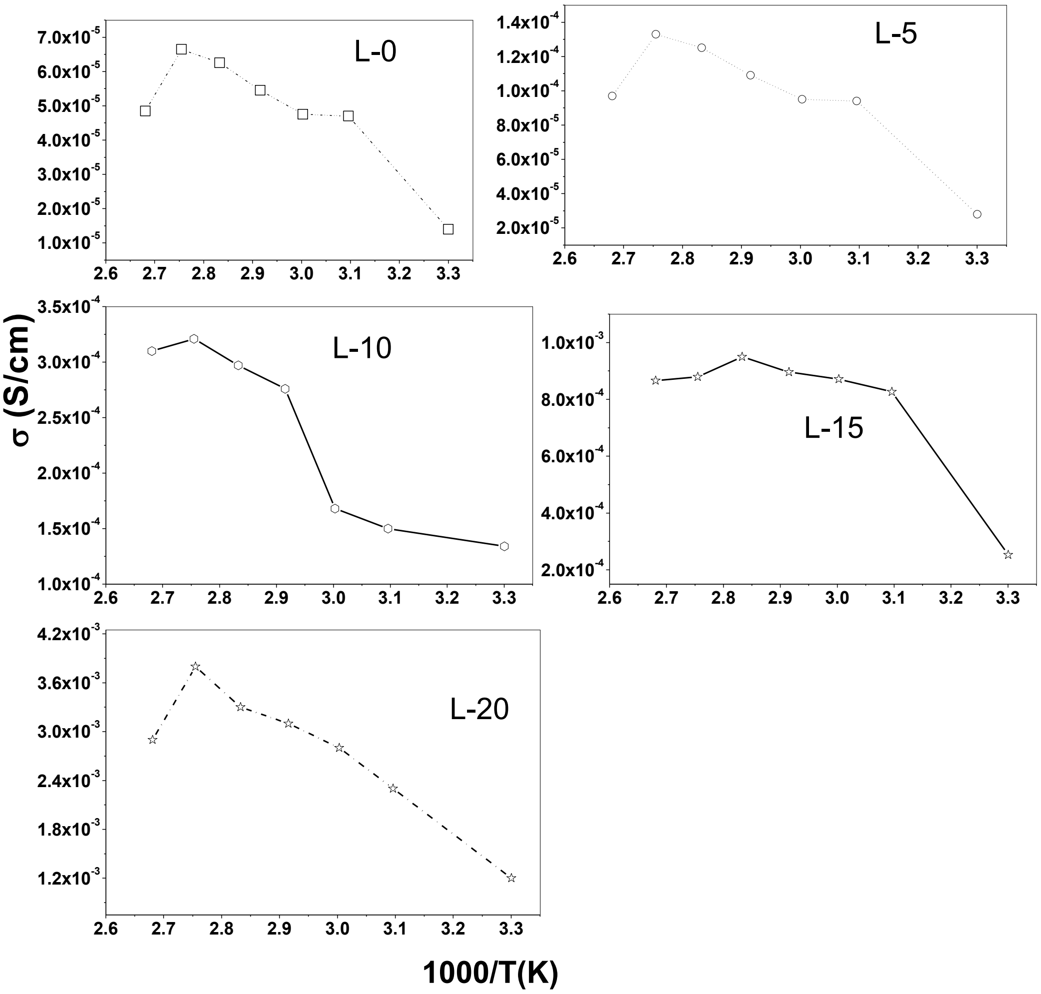
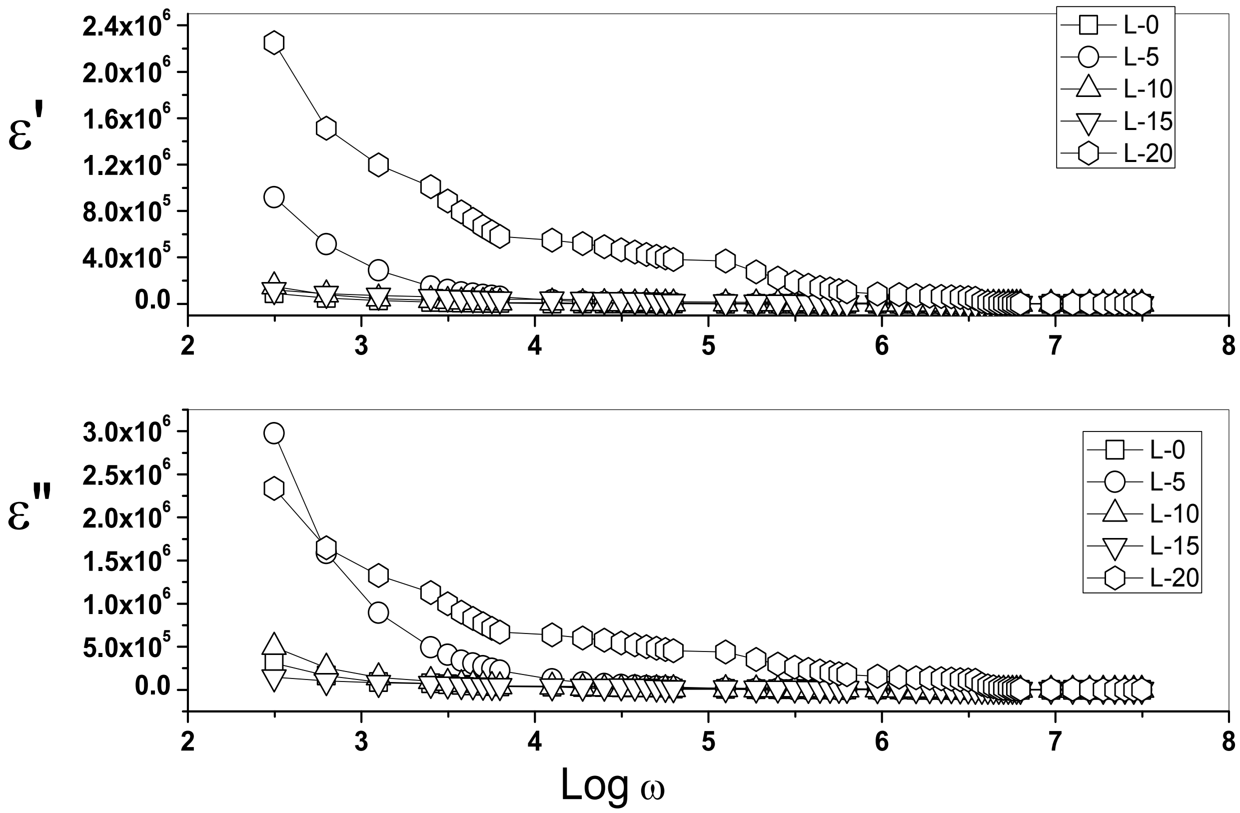
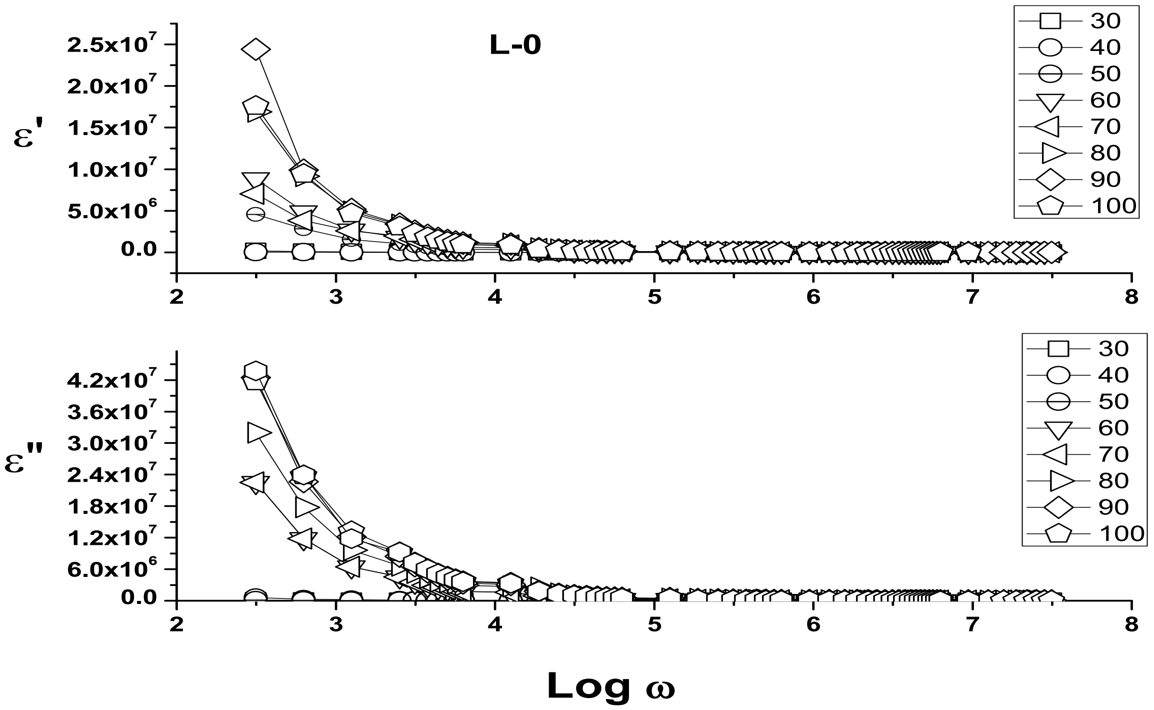
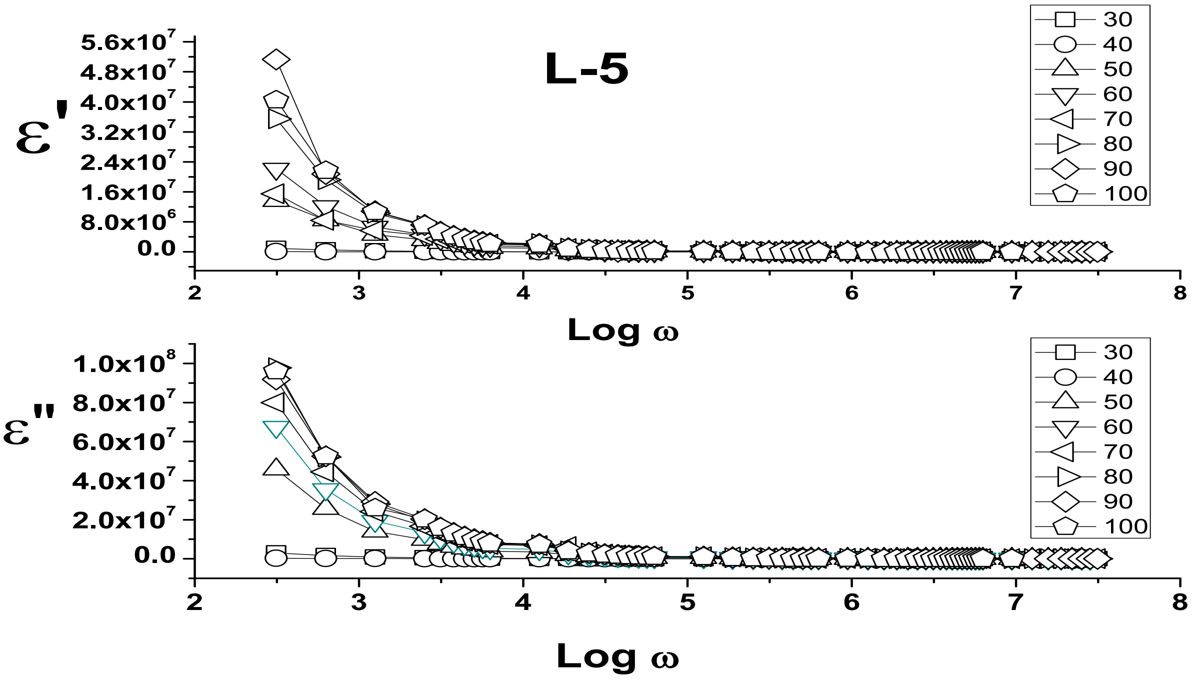
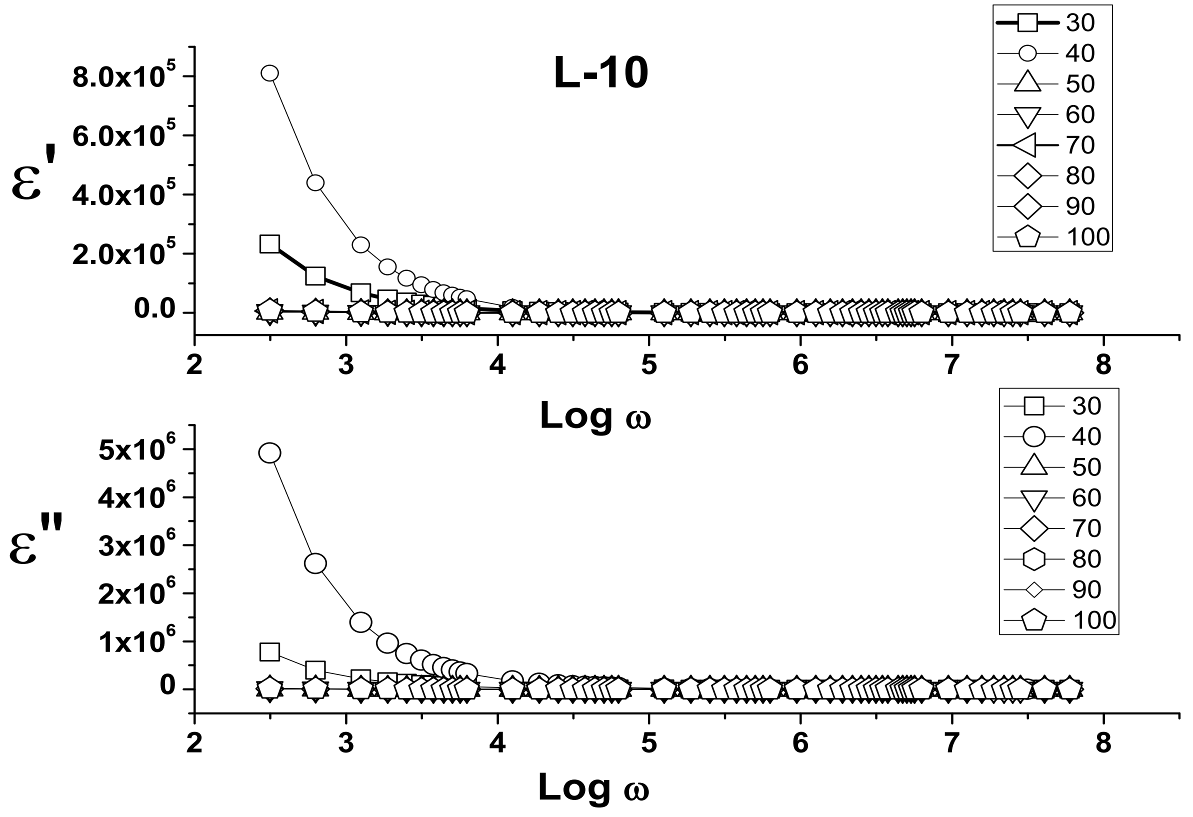


Figure 4 Temperature dependence of ionic conductivity of Starch-PVA polymer electrolytes with different contents of LiBr


ε'
2.4x10^6
2.0x10^6
1.6x10^6
1.2x10^6
8.0x10^5
4.0x10^5
0.0
L-0
L-5
L-10
L-15
L-20
2
3
4
5
6
7
8
ε''
3.0x10^6
2.5x10^6
2.0x10^6
1.5x10^6
1.0x10^6
5.0x10^5
0.0
L-0
L-5
L-10
L-15
L-20
Log ω


L-0
ε'
2.5x10^7
2.0x10^7
1.5x10^7
1.0x10^7
5.0x10^6
0.0
30
40
50
60
70
80
90
100
2
3
4
5
6
7
8
ε''
4.2x10^7
3.6x10^7
3.0x10^7
2.4x10^7
1.8x10^7
1.2x10^7
6.0x10^6
0.0
Log ω


L-5
ε'
5.6x10^7
4.8x10^7
4.0x10^7
3.2x10^7
2.4x10^7
1.6x10^7
8.0x10^6
0.0
2
3
4
5
6
7
8
Log ω
30
40
50
60
70
80
90
100
ε''
1.0x10^8
8.0x10^7
6.0x10^7
4.0x10^7
2.0x10^7
0.0
2
3
4
5
6
7
8
Log ω
30
40
50
60
70
80
90
100


L-10
ε'
8.0x10^5
6.0x10^5
4.0x10^5
2.0x10^5
0.0
2
3
4
5
6
7
8
Log ω
30
40
50
60
70
80
90
100
ε''
5x10^6
4x10^6
3x10^6
2x10^6
1x10^6
0
2
3
4
5
6
7
8
Log ω
30
40
50
60
70
80
90
100

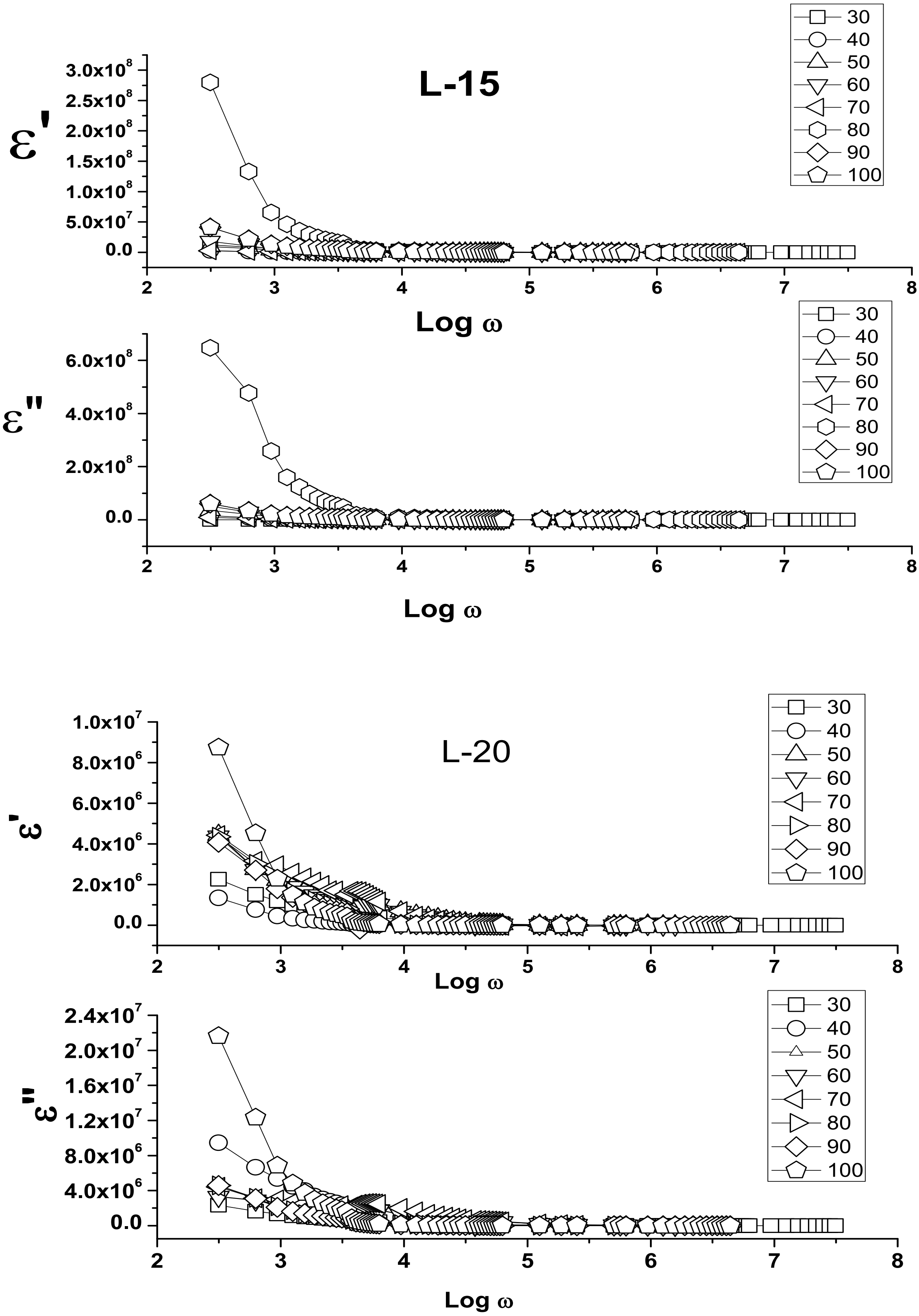
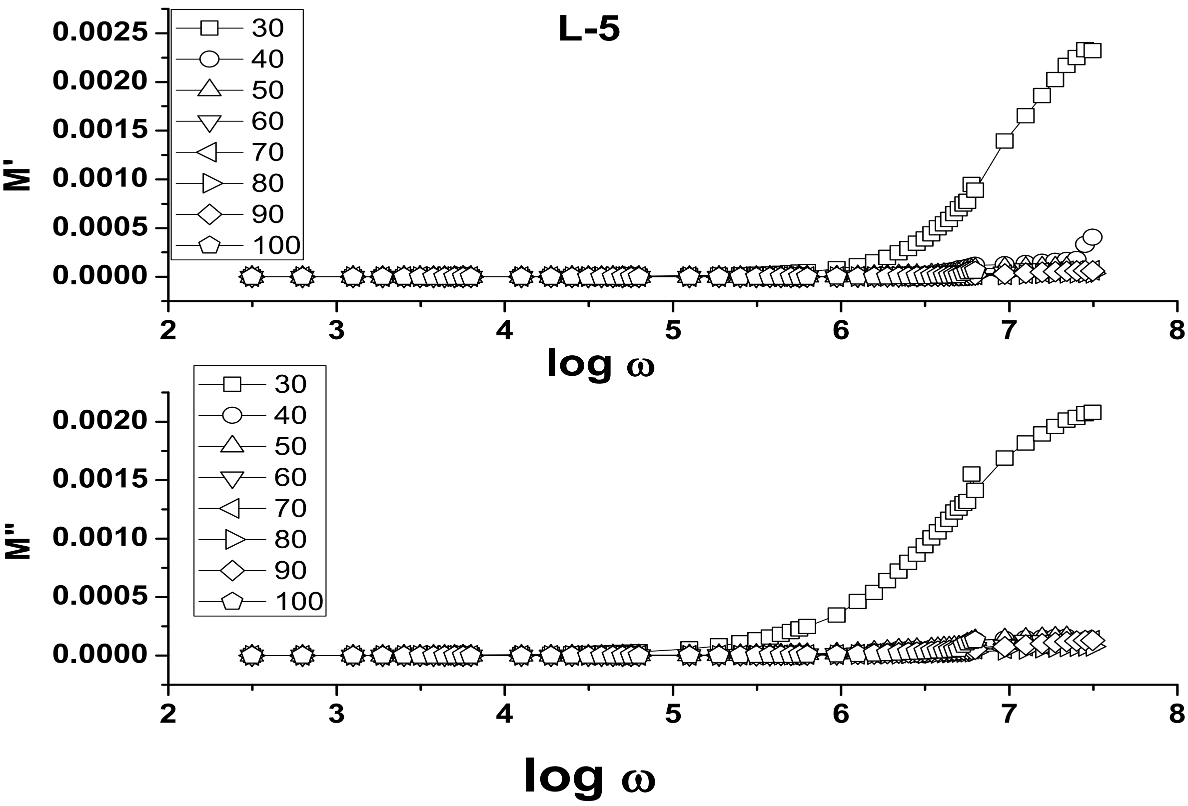
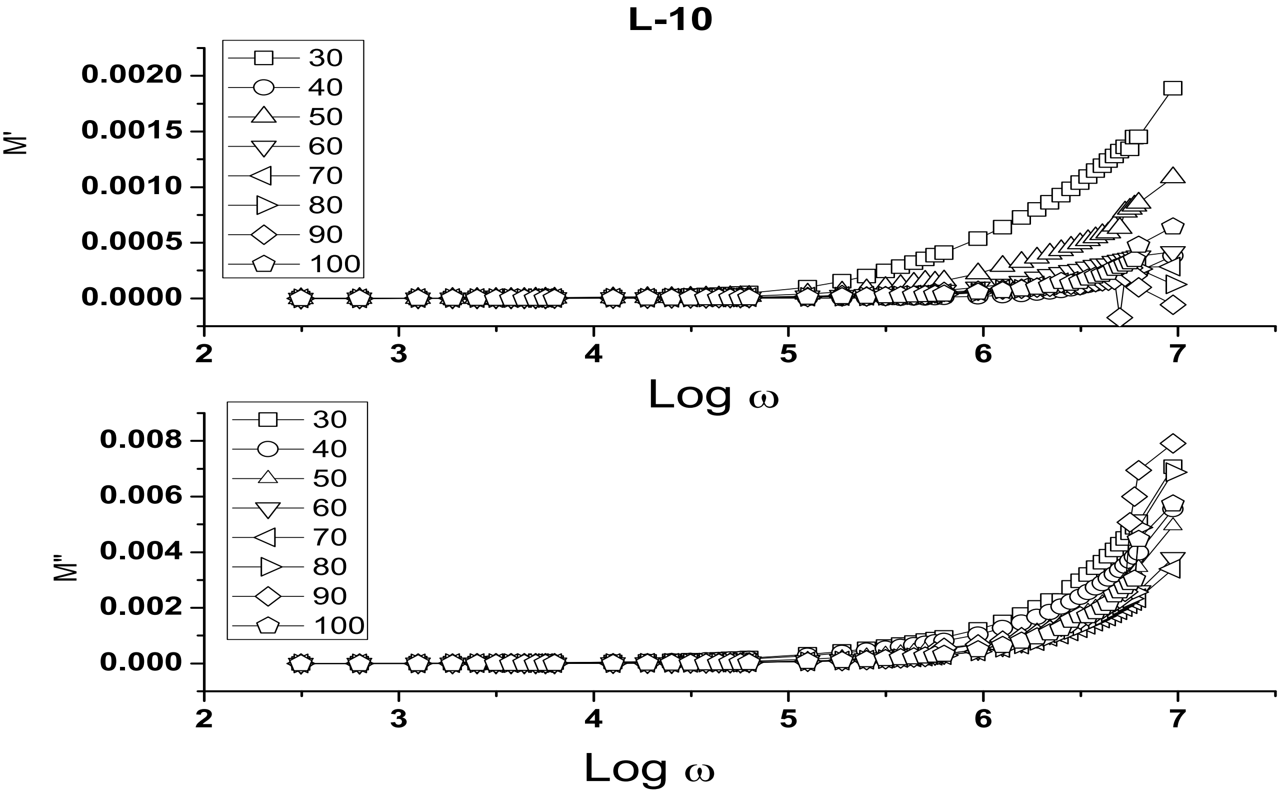
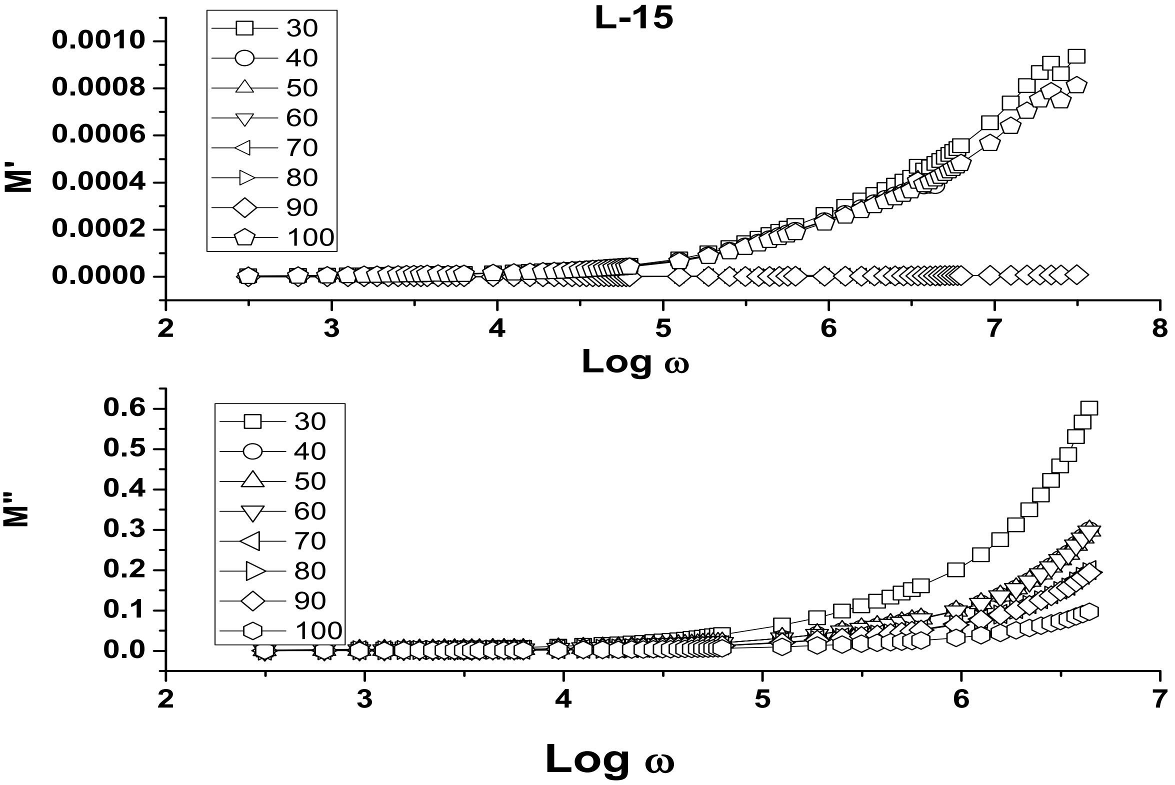


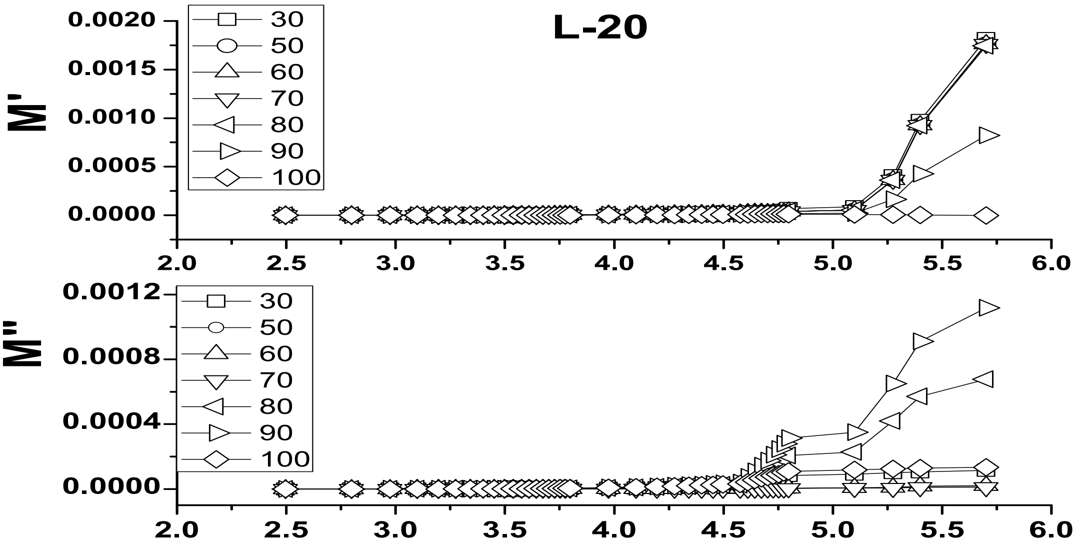
Figure5 (a) Frequency dependent dielectric properties of the Starch-PVA polymer electrolytes with different contents of LiBr at room temperature (b) Frequency dependent dielectric properties of the Starch-PVA polymer electrolytes with different contents of LiBr at various temperatures

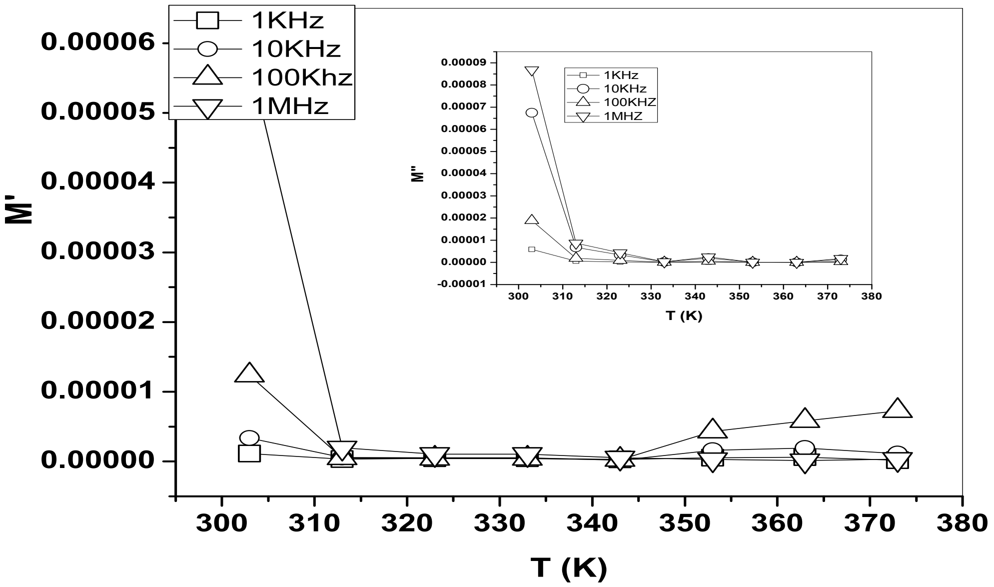

L-5
M'
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
30
40
50
60
70
80
90
100
2
3
4
5
6
7
8
log ω
M''
0.0020
0.0015
0.0010
0.0005
0.0000
30
40
50
60
70
80
90
100
2
3
4
5
6
7
8
log ω


L-10
M'
0.0020
0.0015
0.0010
0.0005
0.0000
30
40
50
60
70
80
90
100
2
3
4
5
6
7
Log ω
M''
0.008
0.006
0.004
0.002
0.000
30
40
50
60
70
80
90
100
2
3
4
5
6
7
Log ω

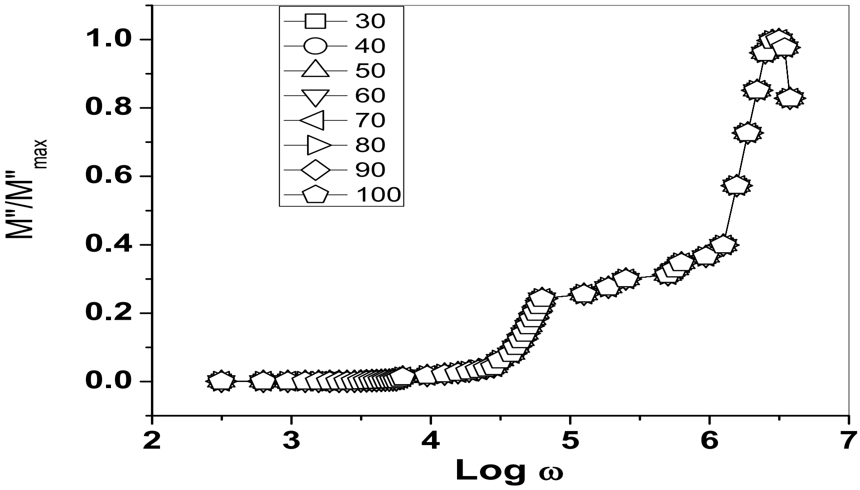

L-15
M'
0.0010
0.0008
0.0006
0.0004
0.0002
0.0000
30
40
50
60
70
80
90
100
2
3
4
5
6
7
8
Log ω
M''
0.6
0.5
0.4
0.3
0.2
0.1
0.0
30
40
50
60
70
80
90
100
2
3
4
5
6
7
Log ω

(a)


L-20
M'
0.0020
0.0015
0.0010
0.0005
0.0000
30
50
60
70
80
90
100
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
M''
0.0012
0.0008
0.0004
0.0000
30
50
60
70
80
90
100
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0



(b)



(C)

Figure 6(a) Electric Modulus spectra of the Starch-PVA polymer electrolytes with different contents of LiBr at room temperature. (b) Inset showing temperature dependence of M' and M" of the sample L-20 at 1KHz,10KHz, 100KHz, and 1MHz (c) Scaling behavior of M" for the sample L-20 at different temperatures.

Table 1: **Variation of activation energy for ionic conduction of the Starch-PVA polymer electrolyte samples with varying contents of LiBr**

Sample	Ea in eV
L-0	**0.175**
L-5	**0.171**
L-10	**0.144**
L-15	**0.154**
L-20	**0.123**