



Investigation of on Lithium Ion-Conducting Blend Polymer Electrolytes Based On PVA, PAN and PVdF

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Abstract: Blending of polymers is one of the most useful methods for synthesizing solid polymer electrolytes. Blend polymer electrolytes have been prepared with Polyvinylalcohol (PVA), Polyacrylonitrile (PAN) and polyvinylidene fluoride (PVdF) doped with lithium nitrate different compositions by solution casting technique using Dimethylformamide (DMF) as the solvent. The prepared electrolytes are characterized by X-ray diffraction analysis (XRD) and AC Impedance techniques. (LCR). XRD shows the amorphous nature of the prepared polymer electrolytes. The ionic conductivity has been found out by the LCR analysis. **The maximum ionic conductivity has been found to be 1.901×10^{-3} (S/cm) at 303K 0.5 M wt% LiNO_3 doped polymer electrolytes.** Dielectric studies are made to know the electric properties of the prepared electrolytes.

Keywords: Polyvinylalcohol, Polyacrylonitrile, Polyvinylidene fluoride, LCR, XRD.

1. Introduction

Polymer electrolytes which have higher ionic conductivity play a major role in the ionic devices viz. electro chromic devices, sensors, and super capacitors[1]. Various methods have been adopted to enhance the ambient temperature ionic conductivity of the polymer electrolyte. One such method is to dissolve inorganic salt in polymer matrix. The polymers like PVA, PAN, and PVdF have been used to develop polymer electrolytes.

Polymer blending is one of the most promising ways by which properties could be changed. Polymer blends are physical mixtures of structurally different polymers that interact through secondary forces and that are miscible to the molecular level. It has attracted much attention as an easy and cost effective method of developing polymeric materials. A polymer blend or polymer mixture is a member of a class of materials analogous to metal alloys in which atleast two polymers are blended together to get a new material with different physical properties[2][3].In the present study, the polymers like PVA, PAN, and PVdF have been used to develop polymer electrolytes.

Poly(vinyl alcohol) (PVA) is a polymer that has been studied intensively because of its good film forming nature, high hydrophilicity, processability, biocompatibility, and good chemical resistance. It is a semi-crystalline polymer, containing crystalline and amorphous phase. Poly vinyl alcohol (PVA) is a cheap polymer having adhesive properties, good chemical and mechanical stability and high potential for chemical cross-linking. However, PVA is highly swelling and has low proton conductivity[2][3][4].

Polyacrylonitrile (PAN) a commercially important polymer is a predominant precursor Activated PAN films can find application as electrochemical supercapacitor electrodes.It absorbs many metal ions and aids the application of absorption materials .Polymers containing amidoxime groups can be used for the treatment of metals because of the polymer complex- forming capabilities with metals ions [5].PAN has properties involving low density, thermal stability ,high strength and modulus of elasticity .These unique properties have made PAN as essential polymer in high tech .Its high tensile strength and tensile modulus are established by fiber sizing ,coatings, production processes and PAN's fiber chemistry .Its mechanical properties derived are important in composite structures for military and commercial aircraft[6][7].

Polyvinylidene fluoride (PVdF) is a polycrystalline polymer started drawing scientific interest in the seventies, because of its extraordinary pyro end piezoelectric properties. These properties combined with both high elasticity and processing ability lend this material numerous technological applications . PVdF has been chosen as polymer host for the present study because of its combination of flexibility, low weight, low thermal conductivity, high chemical corrosion resistance, and heat resistance[8] . Poly (vinylidene fluoride) (PVdF) is a thermoplastic material used in a variety of products and parts such as piezoelectric film, fiber, belt, and pipe. For advanced applications of PVdF, it is highly desirable to enhance and control its physical properties such as thermal stability, mechanical modulus, and electrical conductivity[9][10].

Lithium nitrate salt (LiNO_3) has been chosen for getting good ionic conductivity[11]and properties of Lithium metal has shown great promise as an anode material for high-energy storage systems[13][14], owing to its high theoretical specific capacity and low negative electrochemical potential [15][16].



In the present work LiNO_3 doped PVdF polymer electrolytes have been prepared and subjected to various characterizations such as LCR, XRD.

2. Experimental Details

2.1. Synthesis-Solution Casting Technique

Blend polymer electrolytes are prepared with PVA (M.wt.1,25,000), PAN (M.wt.1,40,000), PVdF of various composition using di-methylformamide (DMF) as solvent by solution casting technique. PVA is stirred in DMF at 80°C for 2 hours and after its complete dissociation, PAN is added and stirred for 1 hour after its complete dissociation, PVdF is added and stirred in PVA, PAN solution at 40°C for 1 hour after which the ammonium salt is oven for solvent evaporation at 70°C for 2 days. After the complete evaporation of the solvent the stand alone films were carefully removed from the petri dishes and sealed in an air tight cover. Samples with concentration ratios (Blend: $x\text{LiNO}_3$), where Blend=0.9PVA:0.08PAN:0.02PVdF and ($x=0.1, 0.2, 0.3, 0.4, 0.5, 0.6$) by weight are synthesized. The samples are characterized by XRD, FTIR, AC impedance technique and UV analyzing technique, Dielectric scanning calorimetry, Thermo gravimetric analysis. IR spectrum has been taken in the range $400\text{-}4000\text{ cm}^{-1}$ at room temperature using SHIMADZU IR Affinity -1 spectrometer. AC conductivity measurements have been performed on HIOKI make LCZ meter in the frequency range 42HZ-1MHZ by applying 1V, and at different temperature ranging from 303K to 343K.

2.2 Characterization Ac Impedance Study

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.

XRD Analysis

The X-ray diffraction pattern (XRD) technique was used for characterization of structure of the electrolytes. The XRD of composites were recorded using Philips X'PERT PRO diffractometer ($\lambda = 1.54060\text{ \AA}$) for incident radiation. The XRD peaks were recorded in the 2θ range from $20\text{-}80^\circ$ [18].

3. Results and Discussions

3.1 X-Ray Diffraction Analysis

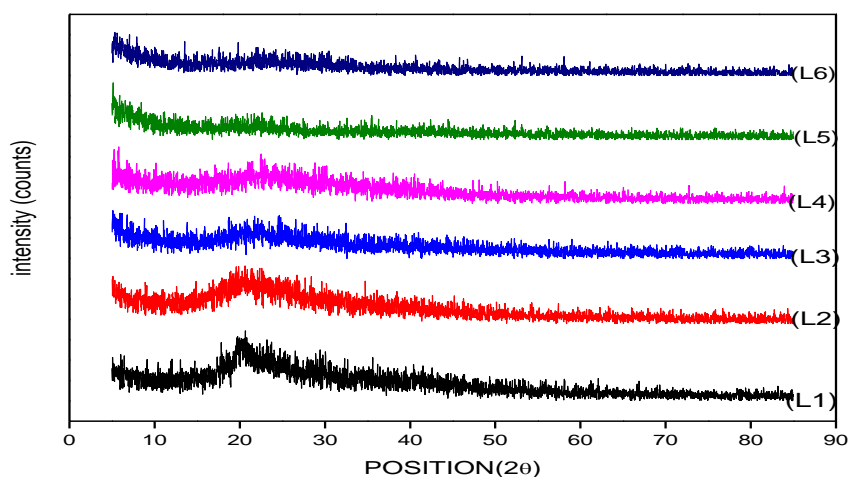


Figure 3.1 XRD pattern of blend polymer electrolyte (L1) 0.1 wt% LiNO_3 , (L2) 0.2wt% LiNO_3 , (L3)0.3wt% LiNO_3 , (L4)0.4wt% LiNO_3 , (L5) 0.5wt% LiNO_3 , (L6) 0.6wt% LiNO_3 of blend polymer electrolytes at 303K.

X-ray diffraction (XRD) studies have been carried out to know the occurrence of complex formation between the polymer and the salt and to know the amorphous nature of the polymer electrolytes[15][16]. In order to understand the properties of composite material, it is essential to know its structure. Figure 3.1 shows XRD spectra (L1) 0.1 wt% LiNO_3 , (L2) 0.2wt% LiNO_3 , (L3)0.3wt% LiNO_3 , (L4)0.4wt% LiNO_3 , (L5) 0.5wt% LiNO_3 , (L6) 0.6wt% LiNO_3 of blend polymer electrolytes at 303K.

From the Figure 3.1, it is seen that a small peak appears at $2\theta = 20.5^\circ$ for L1. Sivadevi et al has shown that the peak at 20.1° corresponding to PVA: PAN blend polymer electrolyte is ascribed to pure PVA[17]. It is also seen



that, as the concentration of LiNO_3 is increased this peak is broadened and its intensity is decreased. Also there is a slight shift in the peak position. For the sample L5, the peak intensity is minimum which shows that L5 is more amorphous than other samples [18]. The peaks corresponding to LiNO_3 are found to be absent which shows the complexation between the polymer matrix and the salt.

3.2 Complex Impedance Analysis

Ac impedance spectroscopy is a powerful experimental tool for characterizing the electrical properties of materials [19][20]. The complex impedance plots (Cole-Cole plots) for blend polymer electrolytes dispersed with figure 3.2.1 (L1) 0.1 wt% LiNO_3 , (L2) 0.2wt% LiNO_3 , (L3) 0.3wt% LiNO_3 , (L4) 0.4wt% LiNO_3 , (L5) 0.5wt% LiNO_3 , (L6) 0.6wt% of LiNO_3 at 303K..

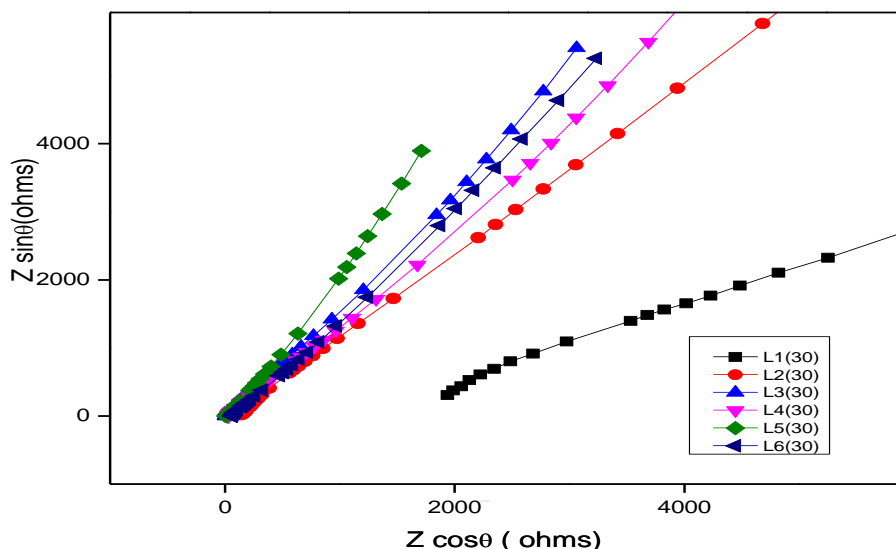


Figure 3.2.1 complex impedance plot of (L1) 0.1 wt% LiNO_3 , (L2) 0.2wt% LiNO_3 , (L3) 0.3wt% LiNO_3 , (L4) 0.4wt% LiNO_3 , (L5) 0.5wt% LiNO_3 , (L6) 0.6wt% LiNO_3 of blend polymer electrolytes at 303K.

The complex impedance plot usually consists of two well defined regions.

- ✓ High frequency semicircle - parallel combination of bulk resistor and bulk capacitor.
- ✓ Low frequency spike -. space charge accumulation at electrode-electrolyte interface.

A high frequency semicircle, which can be related to the parallel combination of bulk resistor and capacitor. The spike represents the formation of double layer capacitance of the electrode-electrolyte interface. The intercept of the spike and the semicircle with the real impedance z' axis gives the bulk resistance (R_b) of the polymer electrolyte [siva devi et al 2013]. The ionic conductivity (σ)

$$\sigma = l/A R_b$$

where l is the thickness of the polymer electrolyte film, A is the surface area of the film and R_b is the bulk resistance of the electrolyte film. In the present study, the semicircle disappears and only the spike is seen. The intercept of the spike with the real axis gives R_b . The highest conductivity at ambient temperature has been found for all the samples.

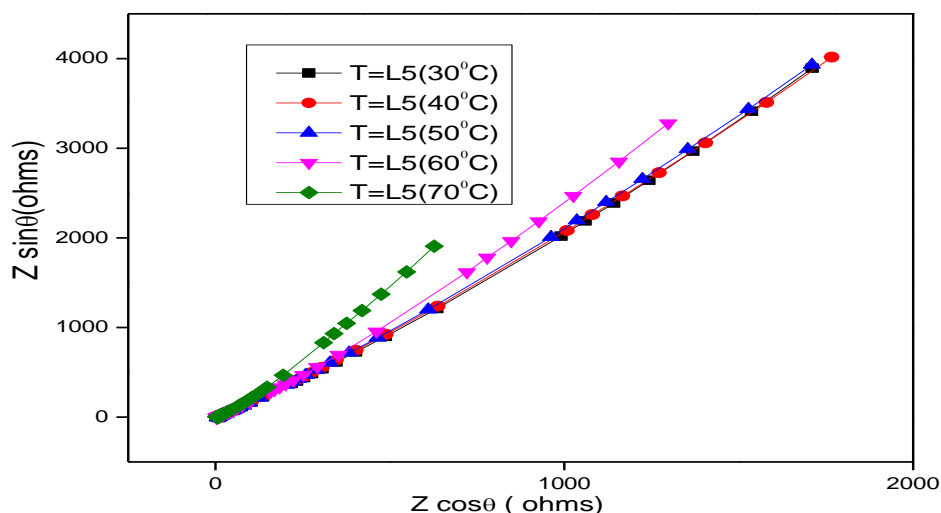


Figure3.2.2 Complex impedance plots of all polymer electrolytes at 303K at different temperatures.

Figure3.2.2 shows that the Complex impedance plots of all polymer electrolytes at 303K at different temperatures.

The decrease in resistance of the polymer electrolyte with temperature is due to the enhancement of the ionic mobility and the number of charge carriers.

3.3 Conductance Spectra

The conductance spectra describe the frequency dependence of the conductivity. The typical $\log \sigma$ versus $\log \omega$ relation for all the samples at room temperature is shown in Figure 3.3.1 (L1) 0.1 wt% LiNO_3 , (L2) 0.2wt% LiNO_3 , (L3) 0.3wt% LiNO_3 , (L4) 0.4wt% LiNO_3 , (L5) 0.5wt% LiNO_3 , (L6) 0.6wt% LiNO_3 , conductivity of LiNO_3 blend polymer electrolytes at 303K respectively. The plot shows a low frequency dispersion region and a high frequency plateau region. Low frequency dispersion region due to the space charge polarization at the blocking electrodes. Frequency independent plateau region representing the dc conductivity.

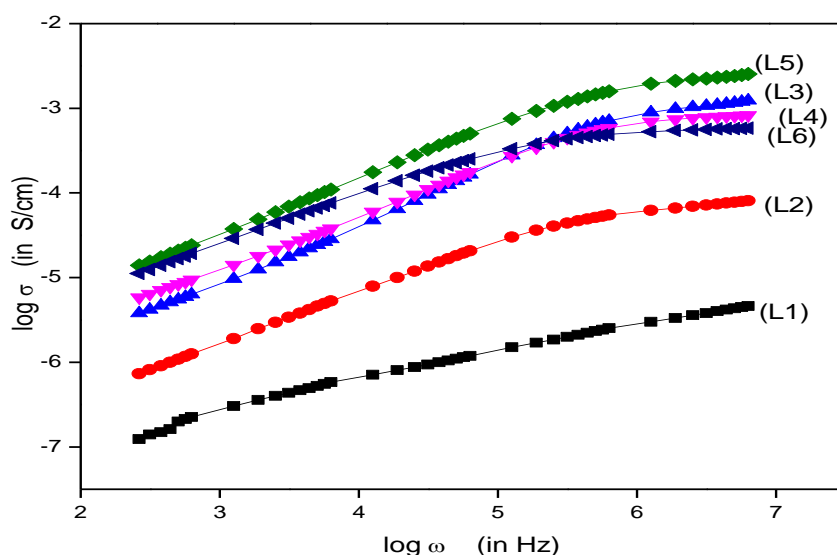


Figure 3.3.1 Conductance Spectra of (L1) 0.1 wt% LiNO_3 , (L2) 0.2wt% LiNO_3 , (L3) 0.3wt% LiNO_3 , (L4) 0.4wt% LiNO_3 , (L5) 0.5wt% LiNO_3 , (L6) 0.6wt% LiNO_3 doped blend polymer electrolytes at 303K.



TABLE:1 Conductivity table from cole-cole and conductance spectra

Sample BLEND: (x) LiNO ₃	Conductivity values from	
	Impedance spectra (Scm ⁻¹)	Conductance spectra (Scm ⁻¹)
Blend:0.1	2.101×10 ⁻⁶	2.971×10 ⁻⁶
Blend:0.2	6.230 ×10 ⁻⁵	6.053×10 ⁻⁵
Blend:0.3	9.725×10 ⁻⁴	9.705×10 ⁻⁴
Blend:0.4	6.825×10 ⁻⁴	6.715×10 ⁻⁴
Blend:0.5	1.910×10 ⁻³	1.901×10 ⁻³
Blend:0.6	5.234×10 ⁻⁴	5.085×10 ⁻⁴

3.3.2 Temperature Dependence of Conductance Spectra for Different Temperature

Figure 3.3.2 shows the conductance spectra the highest conducting sample at different temperatures. It shows three regions: low frequency dispersion region due to the space – charge polarization at the blocking electrodes, frequency independent plateau region corresponding to dc conductivity and the high frequency dispersion region corresponding to bulk relaxation phenomenon. The extrapolation of the plateau to zero frequency gives the value of dc conductivity. It is also seen that the dc conductivity raises with increase of temperature suggesting that the free volume around the polymer chain causes the mobility of ions and polymer segments.[S.Nithya et al 2013].

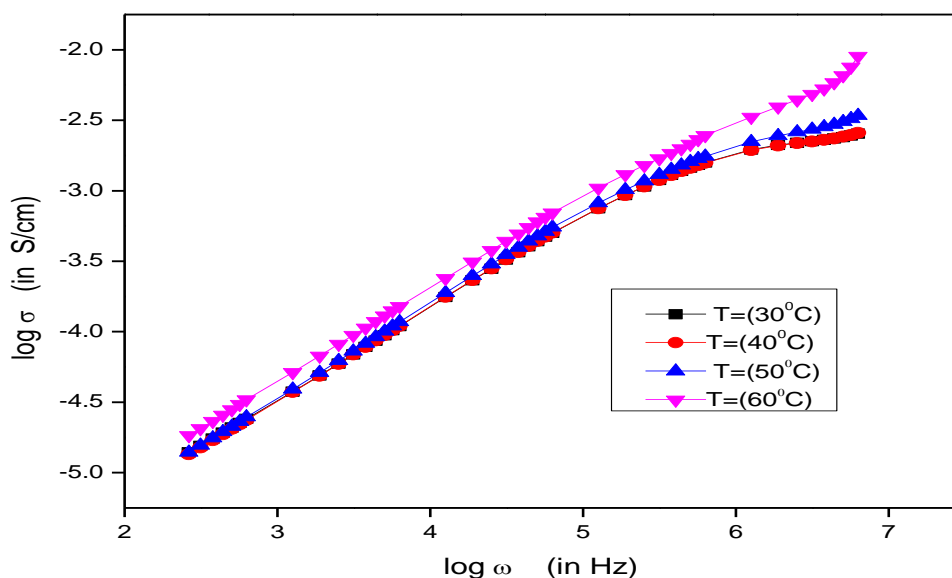


Figure 3.3.2 Conductance Spectra of highest conducting sample at different temperatures.

3.4. Dielectric Studies

The dielectric behaviour of any polymeric system may be reported by the real and imaginary parts of the complex permittivity, ϵ^* which is defined by the relation:



$$\epsilon^* = \epsilon'(\omega) - i \epsilon''(\omega)$$

where real $\epsilon'(\omega)$ and imaginary $\epsilon''(\omega)$ components are the storage and the loss of energy in each cycle of the applied electric field.

Figure 3.4.1 and 3.4.2 represents the frequency dependence of $\epsilon'(\omega)$ and $\epsilon''(\omega)$ (L1) 0.1 wt% of LiNO_3 , (L2) 0.2wt% of LiNO_3 , (L3) 0.3wt% of LiNO_3 , (L4) 0.4wt% of LiNO_3 , (L5) 0.5wt% of LiNO_3 , (L6) 0.6wt% of LiNO_3 , blend polymer electrolytes at 303K, respectively. It has been found that values of $\epsilon'(\omega)$ are high at low frequency. It is due to the presence of space charge effects, which are contributed by the accumulation of charge carriers near the electrodes. The dielectric constant at higher frequencies has been determined to be constant. This is because of the inability of the charge carriers to follow the periodic reversal of the electric field. The large value of $\epsilon''(\omega)$ is attributed to the motion of free charge carriers within the material. Both the values of the dielectric constant and dielectric loss at low frequency have been found to rise with increase in temperature. This is because of the higher charge carrier density. As temperature increases, the degree of salt dissociation and re-dissociation of ion aggregates increases, resulting in the raise of free ions or charge carrier density. [K.P.Radha et al 2013].

3.4.1 Dielectric Studies for All the Samples at Room Temperatures

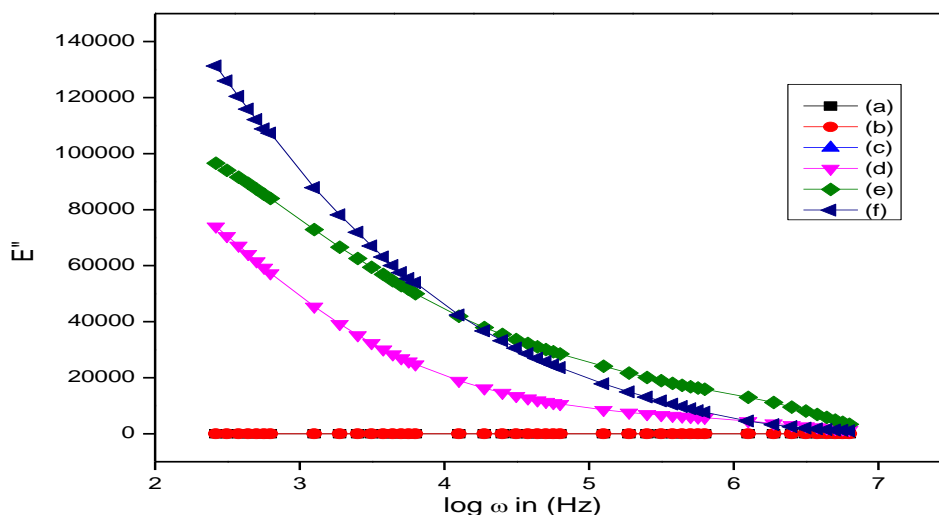
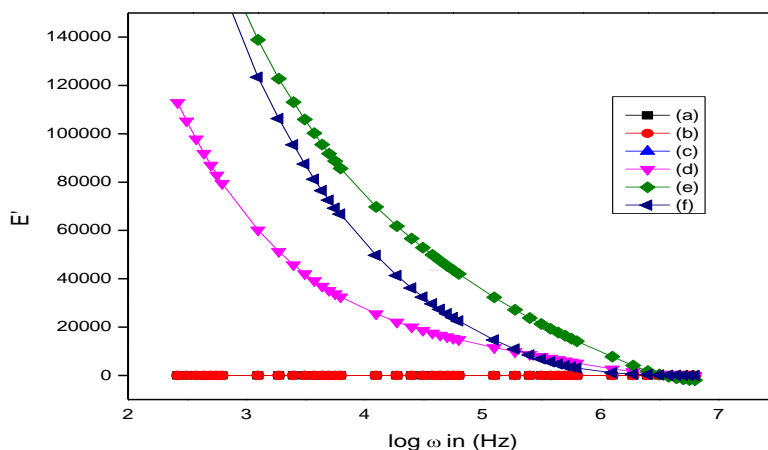
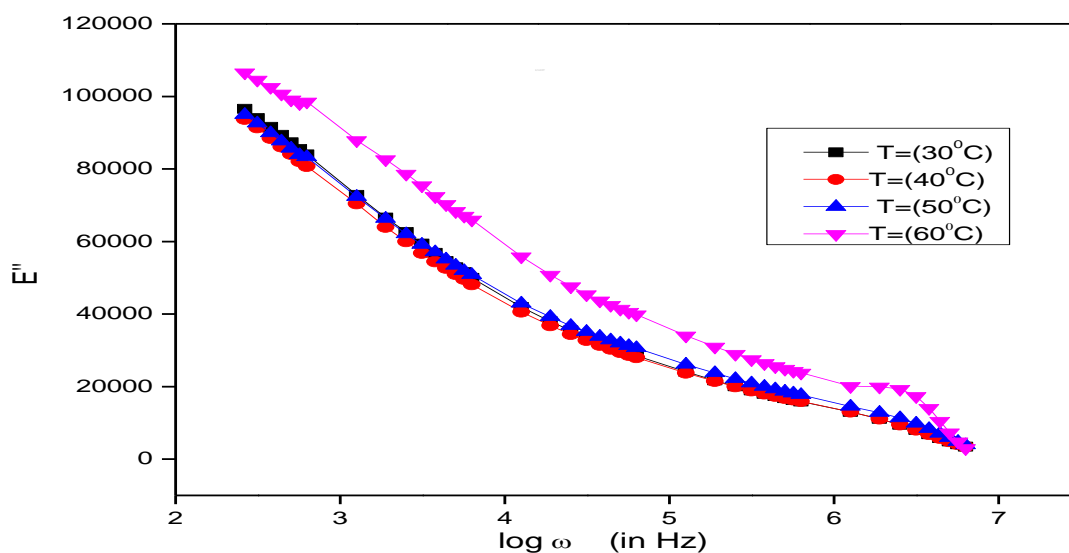
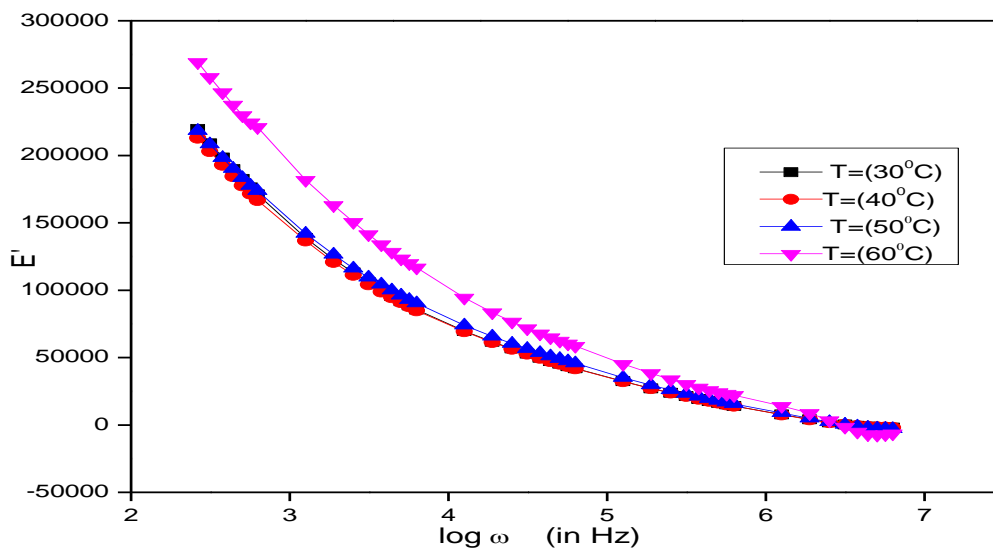


Figure 3.4.(1) and (2) a) 0.1 wt% LiNO_3 , b) 0.2wt% LiNO_3 , c) 0.3wt% LiNO_3 , d) 0.4wt% LiNO_3 , e) 0.5wt% LiNO_3 , f) 0.6wt% LiNO_3 blend polymer electrolytes at 303K .



3.4.2 Dielectric Studies at Highest Conductivity Sample for Different Temperatures

From both the plots it is obvious that the dielectric constant as well as dielectric loss decreases with increasing frequency and are maximum for the highest conducting sample (Blend/weight%).



3.4.(2) Dielectric studies of highest conducting sample for different temperatures.

4. Conclusions

The blend polymer electrolyte with different concentration of Lithium Nitrate have been prepared by solution casting technique. The polymer electrolyte having (Blend) doped with 0.5LiNO_3 and has low bulk resistance and high conductivity of $1.901 \times 10^{-3} \text{ S/cm}$ at 303 K. The structural and vibrational analysis reveal the amorphous nature and complexation of the polymer electrolytes. In dielectric studies it decreases with an increase of frequency and finally reaches nearly a constant value at high frequencies.



5. References

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