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RESPONSE OF CONDUCTIVITY TOWARDS THE CONCENTRATION OF LITHIUM PERCHLORATE SALT IN SOLID POLYMER ELECTROLYTES

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ABSTRACT- The polymer blend electrolytes composed of a fixed ratio of poly (ethyl methacrylate) (PEMA) and Poly (vinyl acetate) (PVAc) and various concentrations of lithium perchlorate ($LiClO_4$) are synthesized by solvent casting technique. AC impedance analysis is carried out to investigate the ionic conductivity of the prepared samples. The maximum ionic conductivity of 3.541×10^{-5} Scm^{-1} at 303K is obtained for PEMA/PVAc (70/30wt%)–$LiClO_4$(8wt%) polymer blend electrolyte system. The XRD and FTIR techniques are adopted to confirm the polymer-salt complexation. The porosity in SEM micrographs is in line with the conductivity measurements. The Glass Transition temperature (T_g) of the blend polymer electrolytes is estimated from DSC measurements and the T_g values agree with the conductivity results. The Linear sweep voltammetry (LSV) analysis is carried out on the polymer electrolyte film of maximum ionic conductivity and shows that the operational potential window of the electrolyte membrane is from -0.8 to +2.8V. The Cyclic voltammetry (CV) is employed to evaluate the electrochemical stability of the polymer electrolyte membrane with 8 wt% of $LiClO_4$. The Lithium transference number measurements are carried out by chronoamperometry technique which reveals that the ion transport is predominant in the prepared sample.

Keywords – [Ionic conductivity; Salt concentration; Free volume model; Glass Transition Temperature; Porosity; Electrochemical stability; Transport number.]

1. INTRODUCTION

Polymer electrolytes in secondary Lithium batteries have drawn considerable attention of the researchers due to its high energy density, light weight, safety, good cyclability and ease of fabrication [1, 2]. There is a growing demand for Li-ion batteries due to its potential applications in the fields of rechargeable batteries and Electrochromic devices [3,4]. However, the polymer electrolytes are to be tuned to exhibit high ionic conductivity, excellent mechanical property and good thermal stability. The requirements are met by adopting various approaches such as the use of cross-linking agents [5] to form networks, use of grafts[6], blending polymers[7], block copolymers [8] and addition of inert fillers to the polymer electrolytes[9]. The reliability of these methods depends on their simplicity and hence blending is the most preferred technique as the physical properties of the blend can be controlled within the compositional regime. The ionic conductivity in polymer electrolytes is mainly influenced by the ionic mobility. As ionic transport occurs mainly through a coupling between the ions and the polymer segmental motion, pioneering work has been carried out to experimentally investigate the properties of polymer- metal salt complexes [10, 11]. Several studies provide information about the type of charge carriers responsible for the conduction.

Among the polymers examined, PEMA has advantageous features such as excellent ionic conductivity, mechanical stiffener, chemical resistance, high surface resistance and offers high optical transparency [12]. Many researchers have blended PEMA with other polymers by exploiting the property of PEMA as a mechanical stiffener to provide a rigid framework in the polymer electrolyte film [13-15]. The polymer PVAc has low glass transition temperature, high melting point and easy film forming property. Also, the polymer PVAc possesses a large dipole moment and high relaxation time [16]. The high amorphous nature of PVAc that aids ionic conductivity in polymer electrolyte systems has attracted the researchers to work on this polymer. The investigation on poly(vinyl acetate) (PVAc) / poly(vinylidene fluoride) (PVdF) polymer blend electrolyte system by Baskaran et.al [17] yielded a high room temperature conductivity of 3.2×10^{-7} S/cm. With the view to improve the ionic conductivity, an attempt has been made in the present work to blend PEMA with PVAc. $LiClO_4$ is used as a dopant salt as it could easily donate lithium ions for ionic conduction in polymer electrolytes due to its low lattice energy. $LiClO_4$ salt has higher anionic radius and aids in ionic mobility. Lithium salts having large anions are suitable for forming polymer electrolytes [18]. When the anions are large, the substantial delocalization of the negative charge occurs with reduction in lattice energy of the salt. Large anions also reduce ion-ion interaction. Thus Li salt with large anions and low lattice energies provide significantly higher conductivity. As the optimal combination of polymer blend and salt plays a vital role in fast ionic transport, optimizing the salt concentration becomes essential.

In the present study, an investigation on the ionic conductivity of PEMA/PVAc polymer blend electrolytes with 5 different $LiClO_4$ salt concentrations is carried out by the AC impedance technique in the temperature range of 303- 353K. XRD and FTIR techniques are adopted to confirm the complexation and the phase structure of the prepared samples. The surface morphology is ascertained from the SEM analysis. The thermal behavior of the polymer blend electrolytes is studied using DSC analysis. The electrochemical behavior of the prepared samples is investigated by Linear sweep Voltammetry (LSV) and Cyclic Voltammetry (CV) measurements. The lithium transference number is estimated using Wagner's polarization method.

2. EXPERIMENTAL TECHNIQUES

Polymer blend electrolytes of various salt concentrations were prepared by solution casting technique. PEMA, PVAc and $LiClO_4$ were purchased from Aldrich (USA) and were dried under vacuum at 100, 80 and 110°C respectively, using Logitech DTC 5050 vacuum oven. The polymer electrolytes were prepared by dissolving appropriate amount of the corresponding constituents in anhydrous THF (E Merck, Germany). The solution was stirred continuously in a magnetic stirrer for 24 h to obtain a homogeneous mixture. The solvent THF in the polymer solution is allowed to evaporate slowly at room temperature for 48 h. To get solvent free films, the films were further dried in vacuum at 60°C for 10 h to remove the residual traces of THF. The obtained films were visually examined for its dryness and free standing nature.

The prepared thin films were subjected to X-ray diffraction (XRD) and Fourier transform infrared (FTIR) studies to identify the crystalline nature and the complexation behavior of the polymer electrolytes using X'pert PRO PANalytical X-ray diffractometer and SPECTRA RXI, Perkin Elmer spectro–photometer in the range of 400 – 4000 cm^{-1} respectively. The ionic conductivity measurements of the polymer complexes in the temperature range of 303-353K were recorded with the help of computer controlled microautolab Type III Potentiostat/Galvanostat in the frequency range of 40 Hz – 300 KHz. Scanning electron microscope (JEOL, IXA-840 Japan) was used for microstructural studies. DSC analysis was carried out using Metler Toledo DSC analyzer.The Electrochemical behavior of the polymer electrolyte film of maximum ionic conductivity is determined by Linear sweep voltammetry and Cyclic voltammetry using Computer controlled micro autolab Type III Potentiostat/ Galvanostat in conjunction with the General Purpose Electrochemical System (GPES). The Lithium transference number t_{Li}^{+} is evaluated by applying a dc polarization pulse to a cell of the SS/polymer electrolyte membrane/SS type using Wagner's DC polarization technique.

3. RESULTS AND DISCUSSION

3.1 X-RAY DIFFRACTION

Fig. 1 shows the XRD pattern of pure $LiClO_4$, PVAc, PEMA and the polymer complexes. The sharp intense peaks at 20.9, 23, 27, 33 and 35° of pure $LiClO_4$ reveal the high crystalline nature of lithium salt. The two broad peaks observed at 14.5 and 22° indicate the amorphous nature of PVAc. The diffraction peaks at 13and 18° correspond to pure PEMA which reveal the semi crystalline nature of the polymer. The diffraction peaks of pure polymers are less prominent in the polymer complexes which indicate the compatibility of the two polymers and confirm that the polymer complexes have switched to amorphous phase as the height of the peaks can be correlated to the degree of crystallinity[19].

The changes in the intensity of the diffraction peaks of the polymer complexes confirm that the polymer undergoes significant structural reorganisation. The disappearance of sharp peaks of $LiClO_4$ in the complexes indicates the complete dissolution of the salt in the polymer matrix. Further the amorphicity of the polymer electrolytes is found to increase with the salt concentration. However, above 8 wt%, there is a drop in the ionic conductivity which may be due to ionic aggregates at higher concentration of Li salt. The ionic aggregates impede the ionic mobility that leads to a decrease in the ionic conductivity. The observed smoothening in the XRD patterns of the polymer complexes from 2 to 8 wt% of lithium salt concentration and occurrence of hump in the XRD pattern of the polymer electrolyte with 10 wt% of $LiClO_4$ justify the conductivity results.

3.2 FTIR ANALYSIS

FTIR is a versatile tool to depict the polymer conformation. The structural and dynamic information of the polymer electrolytes can be extracted from the FTIR spectra. The infra red spectra are the fingerprints of the polymer electrolyte composition which on analysis give details about the complexation within the polymer electrolytes. The mutual interaction between the polymer and the salt generates change in the vibrational modes of their atoms and molecules which in turn is reflected as a remarkable change in the physical and chemical properties of the constituents of the complex.

FTIR spectra of pure $LiClO_4$, PEMA, PVAc and the polymer complexes are shown in Fig.2. The vibrational band observed at 625cm^{-1} is assigned to pure $LiClO_4$. The transmittance peaks at 2940, 2910 and 2085 cm^{-1} are assigned to $–CH_3$ asymmetric stretching, $-C_2H_5$ asymmetric stretching and –CH stretching vibrations of pure PEMA respectively. The peak at 1721 cm^{-1} is ascribed to carbonyl stretching (C = O) in pure PEMA. Also sharp peak at 1485 cm^{-1} confirms the presence of CH_2 – scissoring mode of vibrations in pure PEMA. The appearance of a strong band at 2465 cm^{-1} corresponds to $^{-}CH_3$ symmetric stretching vibration in pure PVAc. The characteristic vibrational bands at 1373, 1243 and 1033cm^{-1} are due to CH_3 symmetric bending, C – O – C stretching and C – O stretching vibrations in pure PVAc respectively.

In Fig.2 it is observed that the vibrational peaks of pure $LiClO_4$ (625 cm^{-1}), pure PEMA (2910, 1721, 1485 cm^{-1}) and pure PVAc (2465, 1373, 1243 cm^{-1}) are shifted to 635, 2920, 1729, 1481, 2473, 1385 and 1253 cm^{-1} in the polymer complexes respectively. The shift in the vibrational bands is due to the interaction between the polymer and salt complex. In addition to shifting of peaks, the absence of peaks of pure polymers is noticed in the polymer complexes. Some new peaks are also found in the complexes. Thus FTIR study confirms the complexation in the polymer electrolyte systems.

3.3 Conductivity measurement

The complex impedance plots of PEMA / PVAc ((70/30) wt %) / $LiClO_4$ (8 wt %) at 303K are shown in Fig. 3. The absence of a semi-circular portion in the AC impedance response curve of samples B3, B4, B5 confirms that the charge carriers in the polymer complexes are ions and the conductivity is purely due to the ionic mobility [20]. The extrapolation of the impedance plot intercept on the low frequency side of the Z´ axis gives the bulk resistance R_b of the polymer electrolyte. The ionic conductivity σ is calculated using the equation,

$\sigma = t / R_b A$

where t is the thickness of the polymer blend electrolyte film, A is the surface area of the film and R_b is the bulk resistance of the polymer blend electrolyte obtained from the complex impedance measurement.

The conductivity values of the polymer complexes in the temperature range of 303 – 353K for various salt concentrations are listed in Table 2. The maximum ionic conductivity value of 3.541×10^{-5} Scm^{-1} at 303K is obtained for the polymer electrolyte with 8wt% of $LiClO_4$ salt. It is observed that as the concentration of $LiClO_4$ salt increases from 2 to 8 wt% there is an increase in ionic conductivity value. This is due to the increase in the charge carrier concentration and hence the ionic mobility. However, beyond 8 wt%, a drop in the conductivity is noticed. At a higher concentration of the salt, the ions group themselves as ion pairs, ion triplets and ionic clouds and thus offset the build-up of charge carriers and restrict the ionic mobility. Thus 8 wt% of $LiClO_4$ in the polymer complex yields maximum conductivity whereas the rise in concentration to 10 wt% hinders the polymer segmental mobility due to ion aggregates. The relative number of effective charge carriers diminishes at equivalent level of segmental mobility at a higher salt concentration [21]. The ionic conductivity as a function of salt concentration is plotted in the Fig. 4. It also shows that at different temperatures the elevated conductivity value is obtained for the sample composed of 8 wt% of Li salt.

The temperature dependence of conductivity is examined by subjecting the prepared samples to impedance measurements in the temperature range of 303–353K. The complex impedance plots of the film (B4) exhibiting maximum conductivity at various temperatures are depicted in Fig. 7. The Arrhenius plot of the polymer complex B4 is shown in Fig. 5. It is evident from the Arrhenius plot that the ionic conductivity increases with the increase in temperature. The temperature dependence of ionic conductivity is explained on the basis of free volume model [22]. As temperature increases, the host polymer expanses and creates local empty space (free volume) into which the ions can move freely. Thus the temperature of the polymer electrolyte decides the free volume availability within the polymer matrix which inturn influences the ionic mobility.

The non-linearity in the Arrhenius plot reveals that inspite of charge carrier concentration; the polymer segmental mobility also plays a vital role on the ionic mobility. The polymer segmental mobility has its influence on the ionic mobility and hence imparts a deviation in the ionic movement and is reflected in the non-linear behavior of the Arrhenius plot [23]. The above mentioned conduction mechanism of ions obey VTF relation given as,

$\sigma = AT^{-1/2}\exp[-B/(T-T_0)]$

Where A and B are constants and T_0 is a reference temperature.

3.4 SEM analysis

Fig. 6 shows the scanning electron microscopic (SEM) images of the prepared polymer complexes. The SEM photographs do not show any phase separation morphology confirming the high compatible nature of the blends. The minimum number of pores observed in the complexes with low concentration of salt is due to the lack of availability of large number of charge carriers. The SEM image of B4 sample exhibiting maximum conductivity shows more number of pores. The appearance of pores is due to the evaporation of solvent in the electrolyte [24,25]. The micropores provide a platform for the hopping of ions. Thus, ion hopping in the polymer electrolytes takes place with the help of micropores and hence porosity can be correlated to the ionic conductivity which go in hand with ionic mobility. The maximum porosity in the SEM micrograph indicates the enhanced ionic conductivity as ions take advantage of the pores for the hopping mechanism. The maximum number of pores observed in the B4 sample is in good agreement with the result observed in the conductivity measurement.

3.5 DSC analysis

Fig. 7 shows the DSC thermograms of the prepared polymer complexes. The DSC analysis helps in ascertaining the glass transition temperature (T_g) of the polymer complexes. The determination of is widely practised as a means of detecting the compatibility in polymer blends. T_g is defined as the midpoint of the steep change in energy. It is a phase change reminiscent of a thermodynamic second order transition. The glass transition temperature is that temperature at which the polymer chain acquires flexibility and the chain begins to exhibit mobility and commences to flow more or less freely. The T_g values of polymer blend electrolytes gradually decreases with increase of salt concentration and is found to be mini mum for 8 wt% of $LiClO_4$. The values of T_g for the polymer electrolytes with various salt concentrations are summarised in Table 3.

The DSC thermograms of the complexes show a single T_g indicating the compatibility of the polymers. The incorporation of $LiClO_4$ salt into the polymer blend matrix decreases the T_g value and hence indirectly pointing out the increase in ionic conductivity. The T_g value is minimum for 8 wt% of salt content. The affinity of salt towards the polymer matrix results in the flexibility of the polymer chain and the extent of relaxation depends on the charge carrier concentration. Thus, polymer segmental mobility enhances the ionic mobility. However, at 10 wt% of the salt content, there is an increase in T_g value which may be attributed to the formation of ion cluster which acts as a constraint for ionic and polymer segmental mobility. The observed Tg values listed in Table 3 correlate well with the conductivity results. The DSC curves depict that all the prepared polymer electrolytes begin to melt around 250° C.

3.6 Linear sweep voltammetry

The investigations on the electrochemical stability window of the polymer electrolyte systems within the operation voltage of the battery system are necessary for practical applications. The electrochemical stability window of the polymer electrolyte system is determined by linear sweep voltammetry [26]. Fig.8 shows the linear sweep voltammogram of the sample exhibiting high ionic conductivity at a scan rate of 100mV/s. The anodic current shoots up at 2.8V may be associated with the decomposition of the polymer electrolyte [27]. The onset of cathodic current observed at -

0.8V is attributed to the electrochemical deposition of Lithium. The electrochemical stability window of the polymer film is found to be -0.8 to 2.8V. No decomposition of the polymer electrolyte is observed within this potential window, thus assuring their use in the Lithium secondary batteries which have a voltage of 3V.

3.7 Cyclic voltammetry

The Fig.9 shows the cyclic voltammogram recorded for PEMA/PVAC ((70/30) wt%)/ $LiClO_4$ (8 wt%) polymer complex at three different scan rates of 25, 50 and 100 mV/S. It is seen that the shapes of the curves almost resemble a rectangle. The increase in the area of cyclic voltammetry plots with the increase in the scan rate indicates that the current is directly proportional to the applied potential. The absence of prominent redox peaks at the anodic and cathodic regions reveals the high capacitive behavior of the polymer electrolyte. The distortion in the rectangular shapes of the curves is found to increase with the scan rates. This is commented on the basis of difficulties confronted by the ionic species in the polymer electrolytes to enter all the vacant sites in the active electrode materials. This may be due to the partial rate of movement of ions in the polymer electrolyte [28].

3.8 Transference number measurements

The Lithium transference number t_{Li}^+ is an important parameter that decides the performance and rate capability of lithium batteries for applications in power tools [29]. Wagner's polarization technique [30] has been used to evaluate the ionic (t_{ionic}) and electronic (t_{elec}) transport numbers. Accordingly a SS/electrolyte membrane/SS is subjected to chronoamperometry by applying a fixed polarization DC potential of 20 mV and the polarization current as a function of time is recorded for 6000s.

Fig. 10 depicts the time dependence of dc polarization measurements at 303K for PEMA/PVAc ((70/30) wt%) / $LiClO_4$ (8 wt%) polymer electrolyte membrane. The lithium transference number has been calculated from the polarization current versus time plot using the equation,

$t_{ion} = (I_i – I_f) / I_i$

where I_i is the initial current and I_f is the steady state current. The Lithium ion transport number is found to be 0.90 for the polymer electrolyte with 8wt% of $LiClO_4$. The value so obtained suggests that the charge transport in the polymer electrolyte membrane is predominantly due to ions. The high transference number is the consequence of the influence of ion-ion and polymer-ion interaction on the macroscopic transport parameters[31].

CONCLUSIONS

1. The Solid Polymer Electrolytes based on PEMA/PVAc with $LiClO_4$ salt at different concentrations are prepared by solution casting technique.
2. The XRD and FTIR techniques confirm the complexation of the prepared samples.
3. The maximum ionic conductivity of 3.541 × 10^{-5} Scm^{-1} at room temperature is reported for the polymer complexes PEMA/PVAc ((70/30) wt%) / $LiClO_4$ (8 wt%) using ac impedance technique.
4. The prepared polymer blend complexes are subjected to SEM analysis. The SEM micrograph of B4 sample shows maximum number of pores which is in good agreement with the conductivity result.
5. The glass transition temperature (T_g) and melting temperature of all samples have been ascertained from the DSC analysis.
6. The polymer electrolyte complex with maximum ionic conductivity is subjected to Linear sweep voltammetry (LSV). The sample exhibits an excellent electrochemical stability window at -0.8 to +2.8V.
7. The Cyclic voltammetry measurements carried out on the B4 sample reveal a good cycling behavior of the electrolyte membrane which may be used as a separator for lithium polymer batteries.
8. The lithium transference number (t_{Li}^+) is evaluated for the polymer electrolyte film with 8wt% of $LiClO_4$ and is found to be 0.90. The high transference number confirms that

the charge conducting species in the polymer electrolyte membrane are predominantly due to ions.

9. Since the free standing polymer electrolyte film (B4) composed of PEMA/PVAc ((70/30) wt%) / $LiClO_4$ (8 wt%) exhibits maximum ionic conductivity and good thermal stability, it may be used in electrochromic devices and battery applications.

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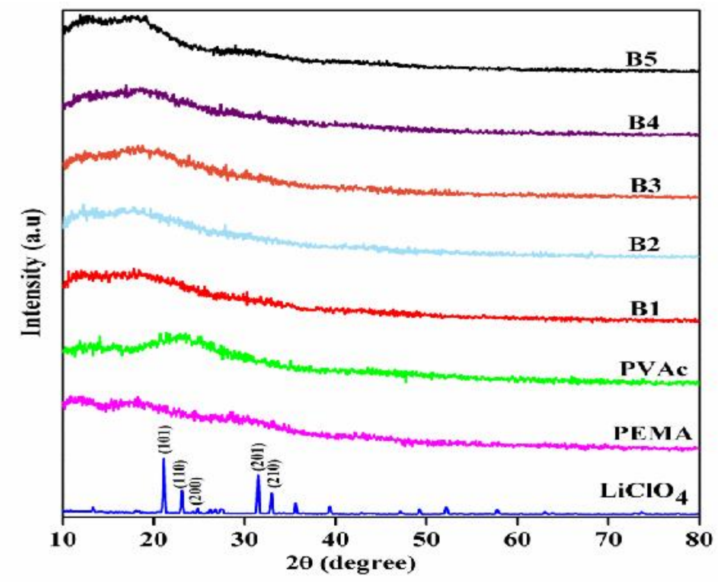

Figure 1- XRD patterns of pure $LiClO_4$, PVAc, PEMA and the prepared complexes.

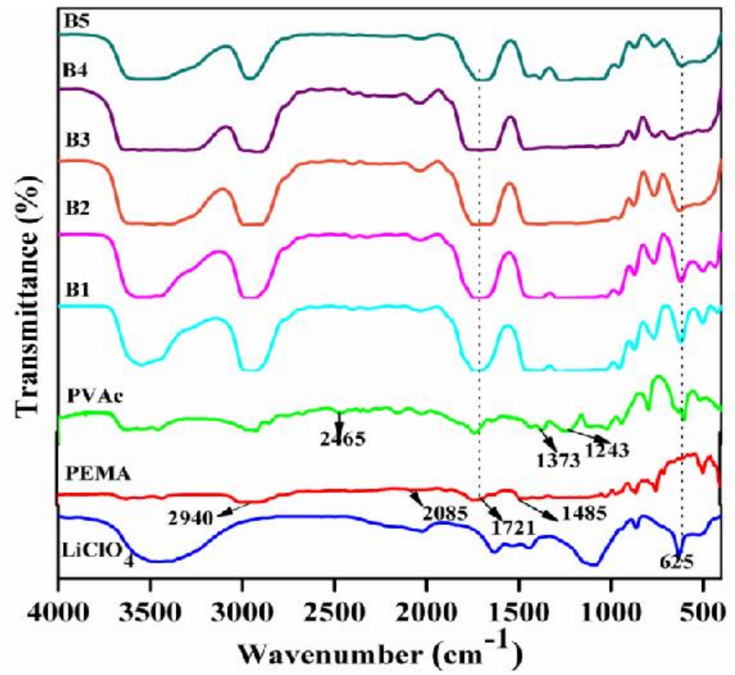

Figure 2- FTIR spectra of pure $LiClO_4$, PEMA, PVAc and the prepared polymer complexes.

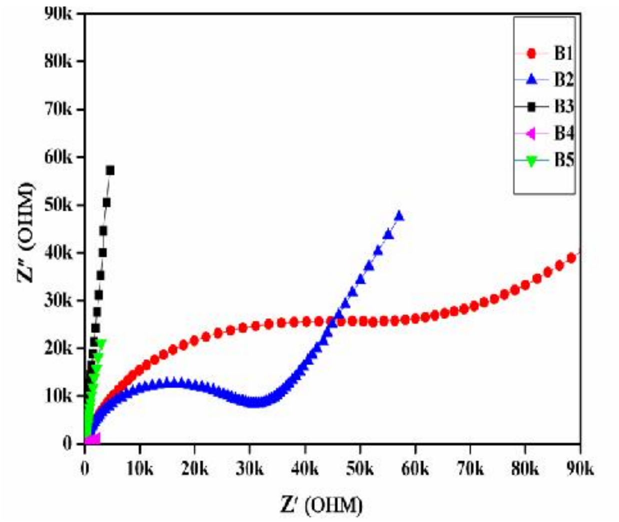

Figure 3- Complex impedance plot of all samples at 303K.

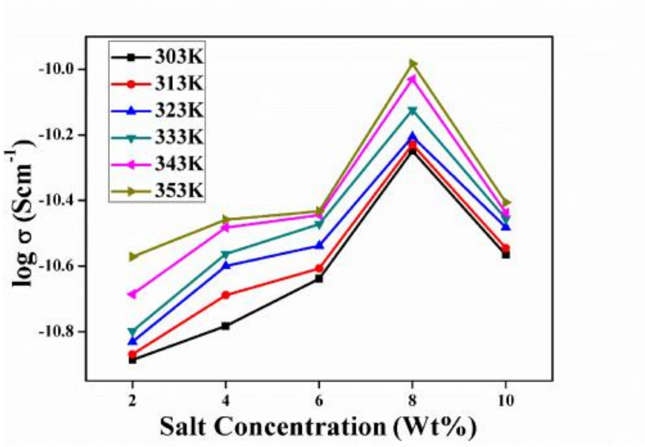

Figure 4- Effect of salt concentration on PEMA/PVAc ((70/30) wt%) /LiClO$_4$ (x) (where x = 2, 4, 6, 8 and 10 wt%) complexes at different temperatures.

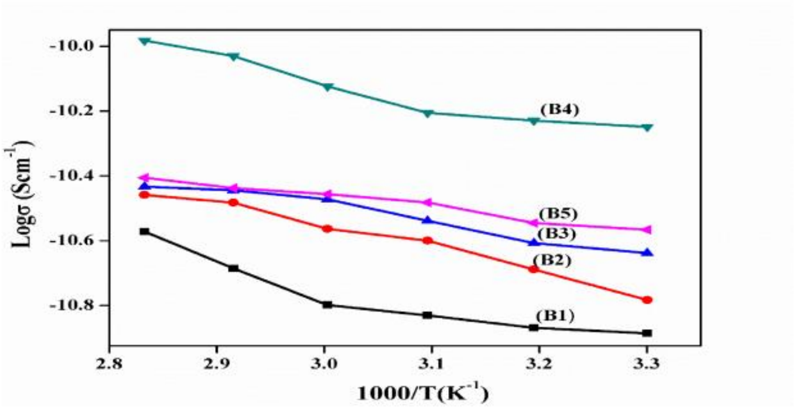

Figure 5- Arrhenius plot of PEMA/PVAc/LiClO$_4$ complexes for different salt concentrations.

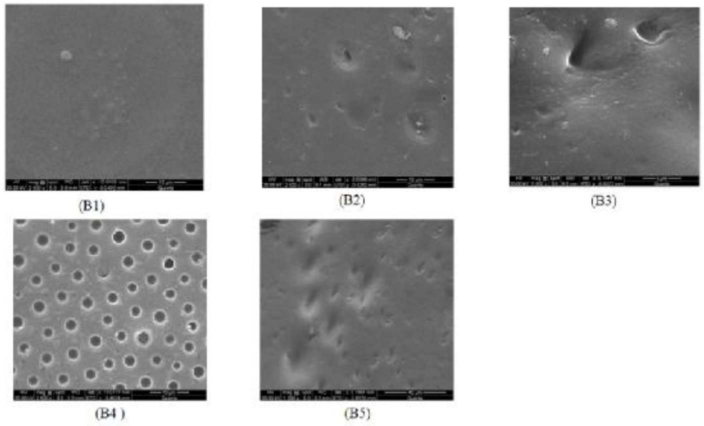

Figure 6- SEM images of the prepared polymer complexes.

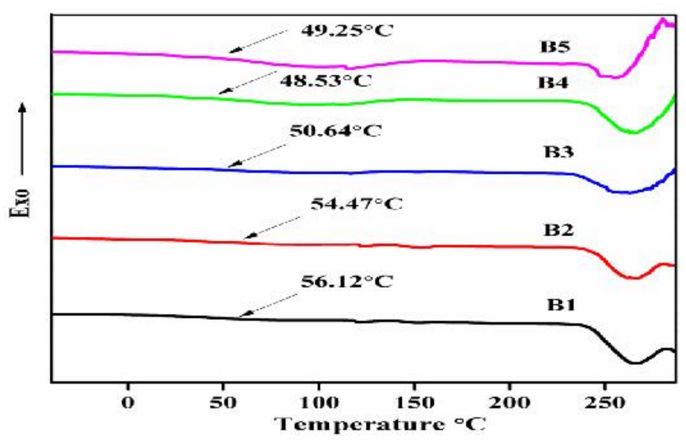

Figure 7- DSC spectra of the prepared complexes.

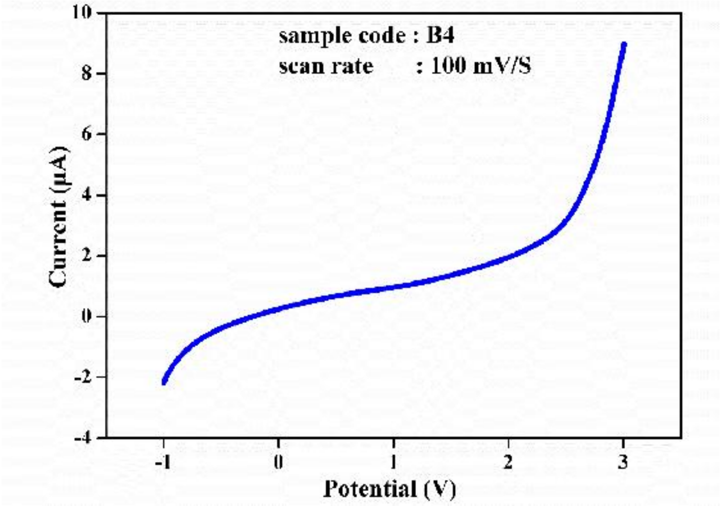

Figure 8- Linear sweep voltammogram of PEMA/PVAc ((70/30) wt%) /LiClO$_4$ (8 wt%) complex at 303 K.

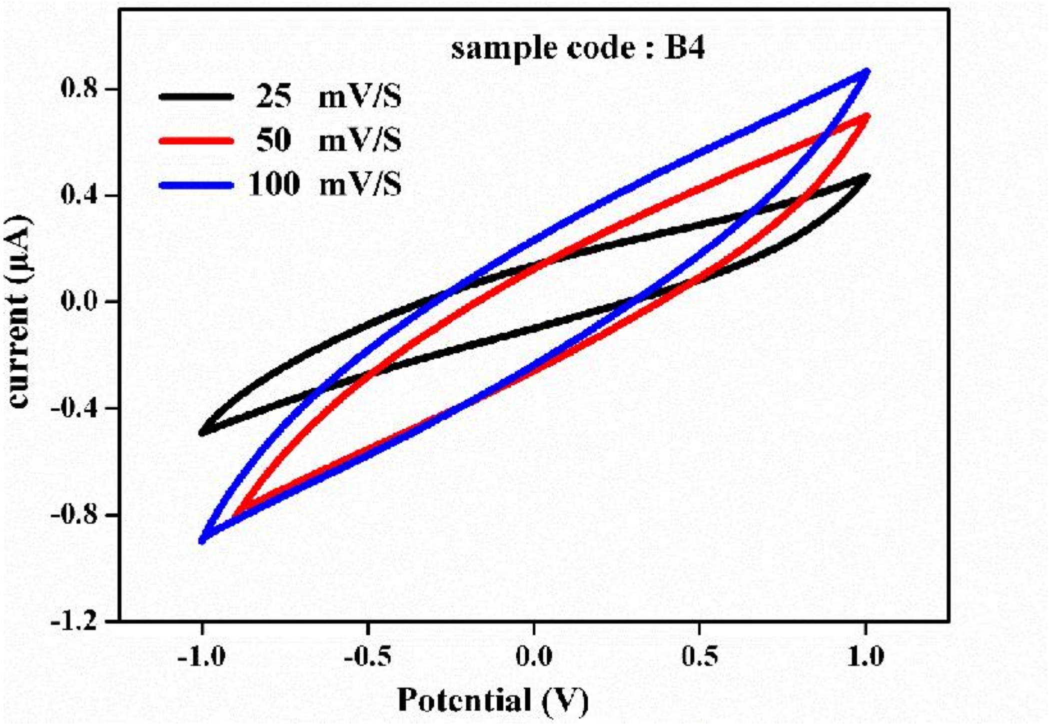

Figure 9- Cyclic voltammograms of PEMA/PVAc ((70/30) wt%) /LiClO$_4$ (8 wt%) complex at 303K.

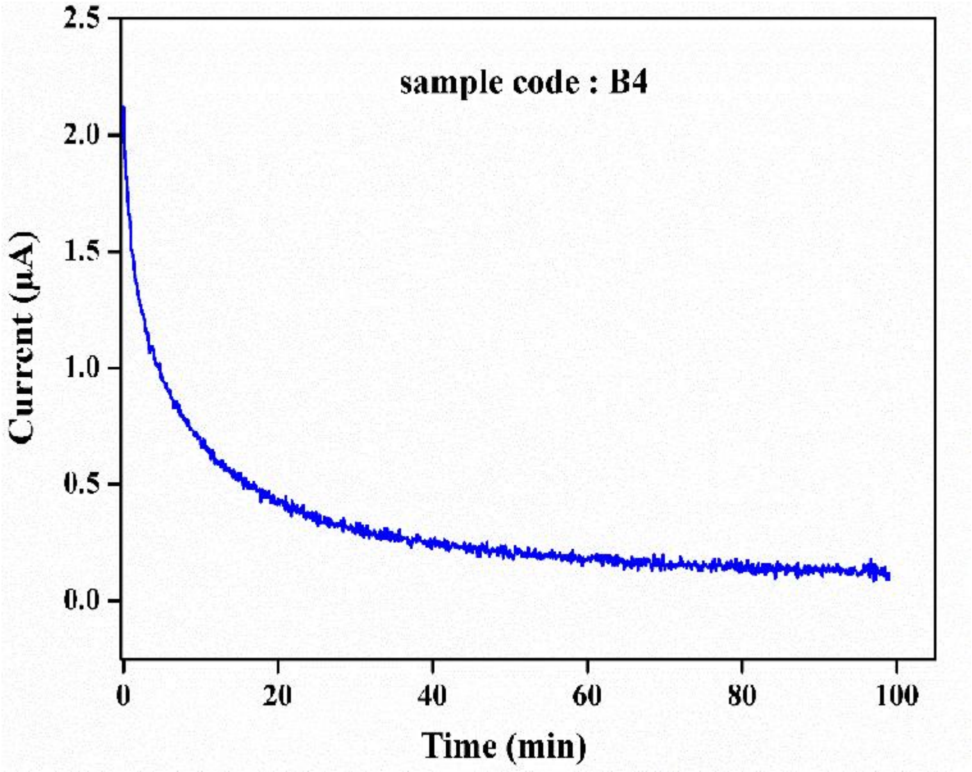

Figure 10- Polarization current as a function of time for PEMA/PVAc ((70/30) wt%) / LiClO$_4$ (8wt%) complex at 303 K.

Band assignments	**Wavenumber (cm^{-1})**						
	PEMA	**PVAc**	**B1**	**B2**	**B3**	**B4**	**B5**
CH_3 (asym. Stret.)	2940	-	2949	2950	2945	2942	2961
C_2H_5 (asym. stret.)	2910	-	2913	2920	2929	2923	2914
CH(stret.)	2085	-	2061	2065	2076	2079	2067
C=O(stret.)	1721	-	-	1733	1738	1729	1734
CH_2(scissoring)	1485	-	1488	1481	-	1482	-
CH_3(sym.stret.)	-	2465	2462	2475	2473	2471	2478
CH_3(sym.bend.)	-	1373	1381	1364	1386	1367	1379
C-O-C(stret.)	-	1243	1245	-	1260	1253	1267
C-O(stret.)	-	1033	-	1042	-	-	1027
ClO_4^-			628	624	637	618	635

Table 1- FTIR spectral data of the prepared samples.

Sample code	**Compositions of PEMA/PVAc/ $LiClO_4$ (in wt%)**	**Conductivity × 10^{-5} Scm^{-1}**					
		303K	**313K**	**323K**	**333K**	**343K**	**353K**
B1	70/30/2	1.872	1.904	1.978	2.043	2.287	2.563
B2	70/30/4	2.075	2.280	2.492	2.585	2.803	2.871
B3	70/30/6	2.398	2.474	2.651	2.832	2.911	2.945
B4	70/30/8	3.541	3.610	3.698	4.012	4.405	4.620
B5	70/30/10	2.578	2.632	2.804	2.877	2.931	3.026

Table 2- Temperature dependent conductivity values of the prepared samples.

Sample code	**Glass Transition Temperature (°C)**
B1	121.66
B2	118.20
B3	111.26
B4	104.33
B5	108.90

Table 3- Glass Transition Temperature of the prepared samples.