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Investigation, Synthesis, Characterization and Detail Studies of Polymer Electrolyte Films of Poly (ethyl methacrylate) with Potassium Iodide as doping salt and Ethylene Carbonate as Plasticizer (PEMA: KI + EC)

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Abstract: *Polymer electrolyte films of poly (ethyl methacrylate (PEMA)) with Ethylene Carbonate (EC) as plasticizer and Potassium Iodide (KI) as ion donating salt was carefully investigated. They were prepared using solution-cast technique with tetrahydrofuran as solvent. The electrical characterization of the films was performed by Impedance spectroscopy for its ionic conductivity and the highest ionic conductivity obtained at room temperature was 1.153 x 10^{-5} Scm^{-1} with the composition of (60:40) PEMA: KI + 10%EC. Ionic transference number of the mobile ions estimated by d.c polarization method and the H^+ ionic transference number was found to be 0.87 which revealed that the conductivity species are predominantly ions. Detailed micrograph of the films was analysed under optical microscopy. The later revealed that both the KI & EC have been uniformly mixed into the polymer host and a good ionic conduction was vividly seen with the optical microscope both in polarized and unpolarized stage. It was concluded that the system PEMA: KI +10%EC is good, and the film can be used for ionic conduction in various application such as electro chromic devices, solar panels, solar cells etc.*

Keywords: *Polymer Electrolyte, Impedance, Optical Microscope, Charge carries, Ion transference number*

I. Introduction

1.1 Ionic conductors.

These are ionically conducting phase which are made/formed by doping a sample salt (which for so long was considered as an insulator) in a solvating polymer matrix through direct interaction of the cation and electron pair. The complex material formed as a result of favourable competition between the solvation energy and the lattice energy of the salt becomes a good ionic conductor. Polymers are usually formed by

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complexing polar polymers like PEO, PPO, PEG, PEMA etc. with ionic salts of monovalent alkali metal-divalent-transition metal ammonium salts [1]. Some salt-free polymer electrolytes have also been reported in which polymer like poly(vinyl alcohol) (PVA) and polyvinylpyrrolidone (PVP) have swollen lattices and anionic solute e.g H_3PO_4 is accommodated for ionic motion [2]. Polysulphonic acid-based polyelectrolyte such as nafion, sodium polystyrene sulphate are also investigated by researchers. Thin film polymer has good properties such as good processibility, flexibility, light weight, elasticity and transparency. Whereas polymer electrolytes have less mechanical strength, workability, time stability, ionic conductivity etc. [2]. In synthesising thin film polymer, the major requirement are the polymer (which acts as the polymer host) and the salt (which act as the ion donating salt especially monovalent salt). Making proper choice of them is very vital in order to have a good film thin polymer satisfying all the necessary requirements.

1.2 Polymer electrolytes

Polymer electrolytes have been a field of great interest in recent decade due to the theoretical as well as practical importance to the development of electrochemical devices. A polymer electrolyte may generally be defined as a membrane that possesses transport properties comparable with that of common liquid ionic solution. The development of polymer electrolytes has drawn the attention of many researchers in the past two decades as they find applications not only in lithium batteries but also in other electrochemical devices such as dye-sensitized solar cell, super capacitors and electrochromic devices [3–8]. These polymer electrolytes have several advantages over their liquid counterparts. Some of the advantages of these electrolytes include but are not limited to; no internal shorting, no leakage of electrolyte, and non-combustible reaction products at the electrode surface.

Polymer electrolytes consist of ionic salts (ammonium, alkali metal salts) in association with polymers such as polyethylene oxide (PEO), poly (ethyl methacrylate (PEMA)), polypropyleneoxide, polyethylene glycol, etc. The first polymer electrolyte was reported in year 1973 by Fenton et al.,[9] in which PEO was associated with potassium and sodium (alkali ion) salts. After that, many polymer electrolytes involving different types of charge species (H^+, Li^+, K^+, Na^+, Ag^+etc.) have been reported. Polymer electrolytes can be prepared by the solution cast technique, sol–gel method, and electrode position method. However, a polymer electrolyte with PEO is the most important polymer matrix because of its high solvating power for the ionic salts as well as low glass transition temperature. Polymer electrolytes based on PEO usually consist of a mixture of crystalline and/or amorphous phases, which significantly play a vital role in the ion transport. Ion mobility is closely related to the segmental mobility of the polymer host/chain and is usually restricted to the amorphous phase. Crystalline polymer electrolytes exhibit mostly low ionic conductivities. Polyethers, polyesters, polyamines, and polythioethers have strong coordinating groups along the chain that can dissolve a variety of salts (especially monovalent ones). The molecular weight of the polymer plays a vital role in the salt complexation and mode of the ion-donating process. In the high molecular weight polymers, the chain wraps around the cation without strain whereas in the low molecular weight polymers solvation of the cation depends mainly on the number of molecules bounded to it. The Lewis acid–base interaction between the solvent and the solute molecules also decides the solvation and dissolution of the salt in the polymer. Another main parameter is the entropy change, which will be considered when dissolving the ion-donating salt in any solvent because after dissolution the entropy will change may be positive or negative entropy of dissolution. In polymer electrolytes, mostly negative change in entropy of dissolution is important at higher temperatures. Owing to the low dielectric constant of the solvent polymers, ion association will reduce the effect of dissociation in entropy. The higher concentration of salt will result in ion association (i.e., ion pairs or higher aggregate formation). In most of electrochemical devices, polymer electrolytes act as electrode separators and provide electronic insulation and fast transport of the desired ions between the electrodes [10–16] obtained, which is viscous in nature.

In the present paper, polymer electrolyte films of PEMA: X wt% KI (where X = 10, 20, 30, 40, 50, 60, 70) were prepared and characterized. To obtain a plasticized film, a fixed amount of EC (10 wt%) was added in all polymer electrolyte films.

II. Materials And Methods

2.1 Material

Poly ethyl methacrylate (PEMA) and ethylene carbonate (EC) was ordered from Sigma- Aldrich, USA, as the polymer host and the ion-donating salt (potassium iodide (KI)) from Qualikem's Fine Chem, Vadodara, India, while tetrahydrofuran (THF) was bought from Qualikem's Fine Chem, Vadodara, India.

2.2 Synthesis Procedure

The solution-casting technique was used to prepare the polymer electrolyte system in the form of film, where the PEMA been the polymer host was dissolved in the solvent (THF), the ion donating salt KI was later added in the solution. Both were stirred separately using a magnetic stirrer for 24hrs, after which the plasticizer (ethylene carbonate) was dissolved (drop wise) in the salt solution first and stirring was continued for 12hrs. This was followed by mixing the two separate solutions together with further stirring for 48hrs to obtain a homogeneous solution (viscous in nature). The homogeneous solution was poured into a polypropylene Petri dish to form a film as a result of evaporation of the solvent (THF). This technique is well known and widely used by the polymer electrolyte community to prepare electrolyte films. The steps involved in the preparation are shown in Figure 1. In the present paper, the polymer electrolyte films of PEMA: X wt% KI (where X = 10, 20, 30, 40, 50, 60, 70) were prepared and characterized. To obtain a plasticized film, a fixed amount of EC (10 wt%) was added in all polymer electrolyte films.

2.3 Characterization

The electrical conductivity measurements of the prepared polymer electrolyte membranes were carried out by A.C impedance spectroscopy technique using a Hioki 3522-50 LCR HiTester in the frequency range 50-100 kHz with a signal level of 10 mV. For conductivity measurements, free standing polymer electrolyte membranes were placed between two stainless-steel (SS) blocking electrodes of 1 cm^2 area. Ion Transference Number (t_{ion}) was measured with Kethlety 2400 source meter. Using the contribution of ions to the total charge transport through the polymer electrolytes by dc polarization method. In this method, a d.c potential of 0.25V was applied across the cell, SS/polymer electrolyte/SS, and the current was recorded as function of time till the complete polarization of the samples. For optical microscopy the Motic BA310 Pol was used in the study of the polarized and unpolarized microscopic image of the polymer electrolyte been synthesized.

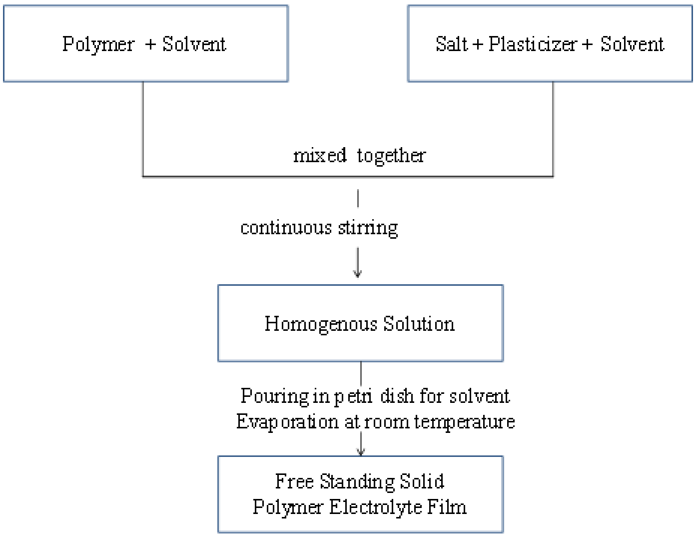

Figure 1: Schematic representation of different steps involve in solution casting technique

III. Results and Discussion

3.1 Ion transference number measurement

The total ionic transference number of the polymer electrolyte casted samples were calculated using Wagner Polarization method. Figure 2 and 3 shows the Polarization current versus time for the two highest conducting polymer electrolyte film in the worked carried out. It shows that the current initially decrease rapidly as the time increases. Initially the current is due to ionic behavior but after a short period of time, the sample becomes polarized, and the current is decreased due to lack of ions. When there were no ions, a very small number of electrons in the sample are responsible for the residual current. The transference number calculated in the present system is 0.87 which shows that the system is mostly due to ionic behavior and is a good candidate for a solid electrolyte. The results obtained is in good agreement with the work conducted by Deraman *et.al* [17] where they reported their work "Conductivity and Electrochemical Studies on Polymer Electrolytes Based on Poly Vinyl (chloride) - Ammonium Triflate-Ionic Liquid for Proton Battery". Their ion transference number tally with the result obtained in this research.

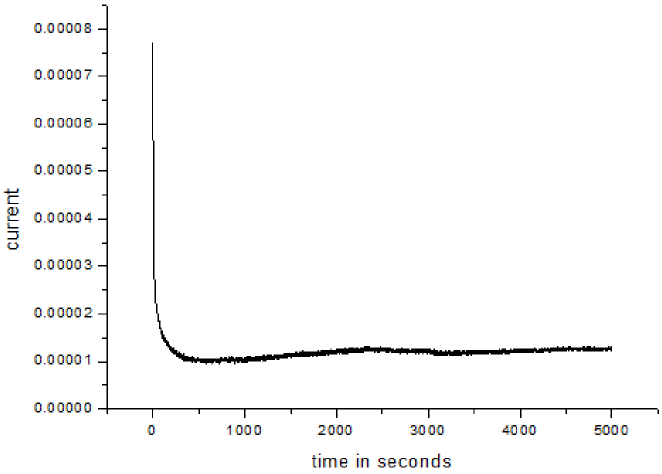

Figure 2: Polarization current versus time for high conducting PEMA:KI+10%EC (70:30)

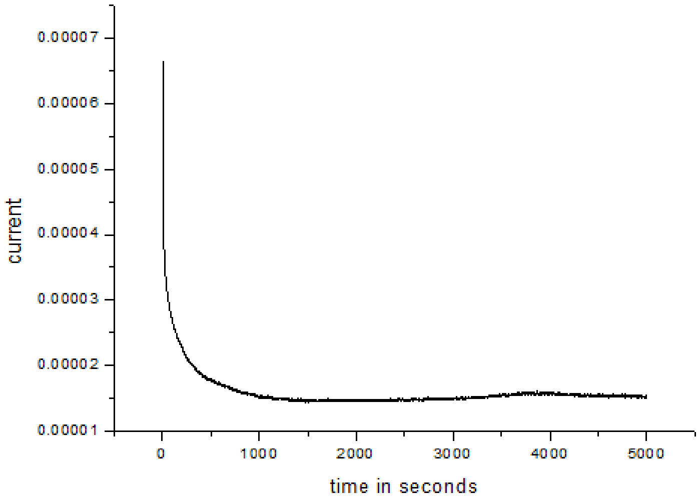

Figure 3: Polarization current versus time for highest conducting PEMA:KI+10%EC (60:40)

3.2 Impedance Spectroscopy

The conductivity of all composition of the system PEMA: KI + 10%EC was taken at room temperature using the ionic conductivity expression in equation 1.

$$\sigma = l/R_bA \qquad (1)$$

Where, R_b is the resistance, l is the thickness of the sample and A is the area of the electrodes and it was found that the composition of PEMA: NH_4I + 10%EC; (60:40) have the highest conductivity of 1.153x 10^{-5}S/cm.

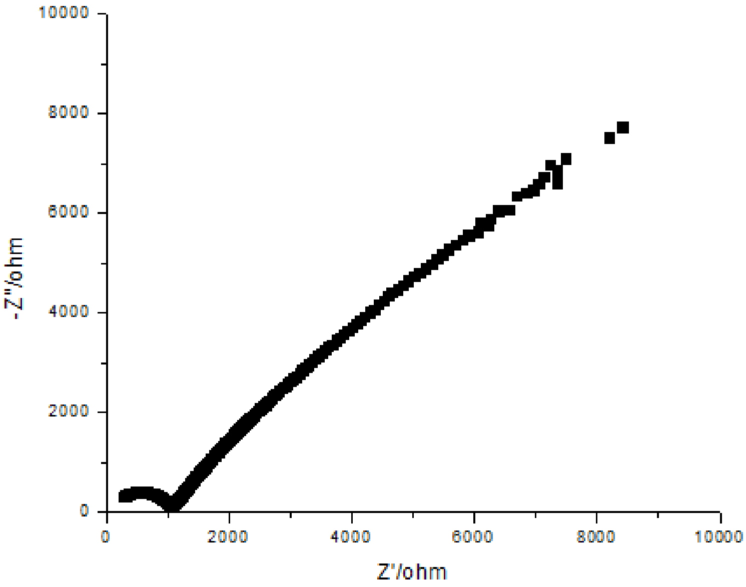

Figure 4: Room temperature complex impedance plot of (60:40) PEMA: NH_4I+10%EC

As shown in Table 1 the first composition of the system have a conductivity of 2.286 x 10^{-6} S/cm as it have less %wt of salt even though the plasticizer have made the film to be mechanically stable. This also is in good agreement with the worked report by Deraman *et.al* [17].

Table 1: Conductivity values of the measured composition

COMPOSITION (PEMA: NH_4I +10%EC)	CONDUCTIVITY (S/cm)
90:10	2.326×10^{-6}
80:20	5.411×10^{-6}
70:30	7.855×10^{-6}
60:40	1.153×10^{-5}
50:50	NIL

3.3 Number of charge carrier

The number of charge carrier(n) was calculated using the values obtained from the plot of dielectric using the equation by Greenbaum *et,al* [18].

$$n = \left(\frac{\sigma_{DC}}{\left(\sqrt{\varepsilon'_{\omega} / \varepsilon'_{s}} - 1 \right) \varepsilon_0 \varepsilon'_s \omega_X} \right)^4 \varepsilon_0 \varepsilon'_s \frac{kT}{e^2 d^2} \qquad (2)$$

Where σ_{DC} is the conductivity at high frequency; ε_0 is the vacuum permittivity; *k* is the Boltzmann constant; *e* is the charge of the electron; ε'_s and ε'_{ω} are the real permittivity at high Frequency and at the frequency ω respectively; and *d* is the thickness of the sample. In the figures of dielectric and the conductivity values obtained directly from impedance measurements which are also shown in Table 1, It can be seen that the increase in conductivity is dominated by increase in the charge carrier concentration as shown in Table 2.

Table 2: Charge density carriers of the various films casted

Composition [PEMA:KI + 10%EC]	Number of charge carriers n (m^{-3})
90:10	3.01×10^{19}
80:20	6.20×10^{19}
70:30	3.10×10^{20}
60:40	1.75×10^{21}
50:50	NIL

The results obtained showed the overall system is an ionic conductor which increases its conductivity with increase in salt content. The increases in mobile charge carrier correspond with the work reported by Bandara *et al* 2011 [19] who worked on "Mobile charge carrier concentration and mobility of a polymer electrolyte containing PEO and $Pr_4N^+I^-$ using electrical and dielectric measurements".

3.4 Dielectric relaxation study

Dielectric formulism is useful in revealing many particulars about conductivity behavior of any material. The dielectric constant is a measure of stored charge. Figure 5 depict the graphs of the dielectric study of the various composition of the thin film casted using equation 3.

$$\varepsilon' = \frac{(-Z''/Z'2+Z''^2)\times 1}{\omega C} \qquad (3)$$

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

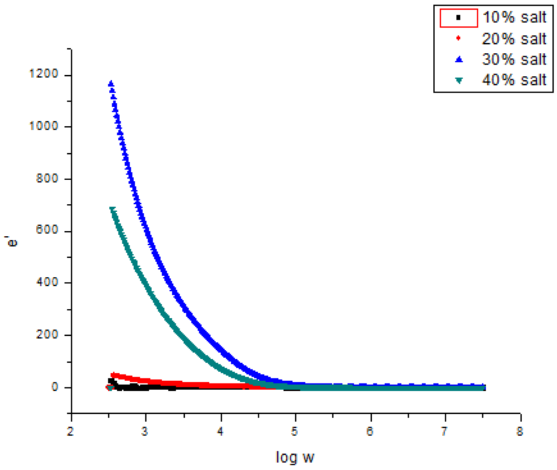

Figure 5: Variation of real part of dielectric constant of all the different composition system of the film casted

From Figure 5, in general we say the dielectric constant increase with decreasing frequency. This is attributed to the high contribution of charge accumulation at the electrode–electrolytes interfaces. At higher frequencies the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. Hence the polarization due to charge accumulation decreases and results in a decrease in the dielectric constant. Increase in the dielectric constant with temperature can be attributed to increase in charge carrier density due to the increase in dissociation of ion aggregates. The results reported in the present study corresponds with the work of Tripathi *et al* [20] who worked on "Studies on electrical conductivity and dielectric behaviour of PVdF–HFP–PMMA–NaI polymer blend electrolyte".

3.5 Optical microscopy structure

Typical recorded micrographs of the polymer electrolyte are shown in Figure 6. Figure 6(a) depict good amount of amorphous structure and big holes/pores which are not helping in the conductivity of the composition but as the EC has been fixed, the system composition is seen with white routes which confirmed that the EC have completely entered the polymer host. Looking at Figure 6(b) micrograph, there is little disappearance of those big pores, like Figure 6(a) the presence of white route depicting EC presence in the polymer host are all over the entire structure. However, the salt content has increased as further confirmed by the color of the micrograph change from yellowish to yellowish-light brown, this confirmed that there is increase of salt content throughout the composition. In Figure 6(c) micrograph, the pores/holes have also reduced as compared to Figure 6(a) and (b) due to the increase of salt content, the color has entirely changed given a light brown color and the present of EC in the system is indicated by the white routes.

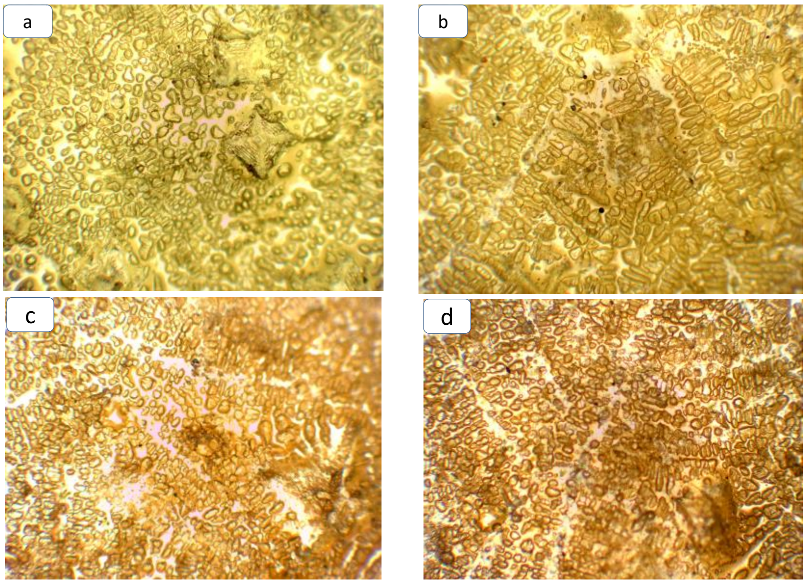

Figure 6: Optical micrograph of the (a) 90:10 "PEMA: KI+10%EC, (b) 80:20 "PEMA: KI+10%EC, (c) 70:30 "PEMA: KI+10%EC, and (d) 60:40 "PEMA: KI+10%EC with 10X magnification

This white routes and lesser holes size go hand in hand with the conductivity that is why the conductivity increases gradually as they salt content increases in the individual system, as such there is increase ionic conduction. Figure 6(d) pores/holes are smaller than all. There ion donating salt have completely dissolved in the polymer host as well as the EC. This explains it darkness compared to the other micrograph(s) and the white color indicate the transfer of ions from one point in the polymer matrix to another which led to more ionic conduction.

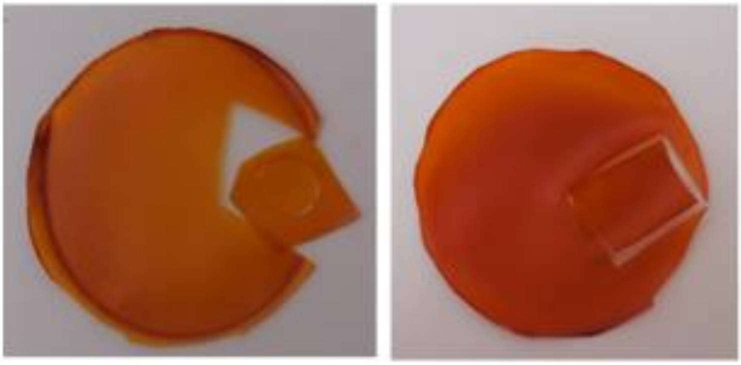

Plate 1: Pictures of film synthesized during the work

IV. Conclusion

The optical microscopy has shown that the film had a very good mixture and both the KI & EC have been uniformly mixed into the polymer host with good ionic conduction vividly seen with the optical microscope both in polarized and unpolarized stage. It is concluded that the system PEMA: KI +10%EC is good and the film can be put to use for ionic conduction in various applications such as electro chromic devices, solar panels, solar cells etc.

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