

# Preparation, Characterizations and Conductivity of PEO-PMMA Based Polymer Blend Electrolyte for Lithium Ion Battery

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**ABSTRACT:** In the present work we have prepared a polymer blend electrolyte comprising of poly (ethylene oxide) PEO, poly (methyl methacrylate) PMMA and LiClO<sub>4</sub> as filler. The polymer blend electrolyte was developed as a film by solution casting technique, with varying ratio of the filler. X-ray diffraction (XRD) revealed that the incorporation of LiClO<sub>4</sub> ions into the blend suppresses the crystallinity of PEO. The SEM studies showed that the particles are spherical, ranging in size from 35-95µm. The ionic conductivity was maximum for 5 wt% of the blend at the ambient temperature.

**KEY WORDS:** polymer blend electrolyte; miscibility; crystallinity; complexation, conductivity, XRD.

## I. INTRODUCTION

Solid polymer electrolytes have attracted attention since more than three decades due to their practical applications as well as for fundamental knowledge [1][2]. Many researchers have worked on several host polymers e.g. poly (ethylene oxide) (PEO), poly (methyl methacrylate) (PMMA), poly (vinyl chloride) (PVC) and poly (vinyl acetate) (PVA) etc. Among various homo-polymers studied, poly (ethylene oxide) (PEO) exhibits excellent ion transport properties due to its high concentration of electron pairs and rapid segmental dynamics. PEO attains high degree of crystallinity, approximately 60%, at room temperature [3-5]. As the amorphous phase is the major contributor to the conductivity, then reducing the degree of crystallinity of PEO-salt systems becomes a unique design objective for which various fruitful efforts have been reported. These studies generally incorporate the development of PEO-based electrolyte composites, copolymers, and blends [6-8]. Polymer blends offer a practical and efficient way to fulfill novel requirements for material properties and applications. Physical properties of polymer blends can be constantly varied among those of the pure components without synthesis of new materials. PEO-based miscible blends such as PEO/PMMA have attracted much attention in recent studies [9-11]. Rigid PMMA chains provide sufficient mechanical stability for the soft PEO segments to achieve improved mechanical performance for solid-state electrolyte applications. Therefore, PEO/PMMA miscible blend can be considered as an interesting candidate for use as electrolyte in solid-state lithium batteries. In this work, effect of adding salt such as LiClO<sub>4</sub> on the structural, thermal behavior, conformational changes were investigated. Further the ionic conductivity of PEO in the dynamically asymmetric miscible blend of PEO/PMMA/LiClO<sub>4</sub> is reported.

## II. EXPERIMENTAL METHOD

### *Materials and Methods*

PEO and PMMA were purchased from Aldrich. The polymers were dried in vacuum for 24 hrs keeping in desiccators. Lithium perchlorate (LiClO<sub>4</sub>) with purity 99.9% was supplied by Aldrich and dried under vacuum oven at 80 °C for 24 hrs. The composition of PEO/PMMA blend was 70/30 wt% and LiClO<sub>4</sub> was added to this blend at different weight percentages viz 1, 2, 3, 4, and 5. Mixtures were prepared by dissolving three components separately in tetrahydrofuran (THF) and stirred for 12 hrs by using magnetic stirrer. PEO/PMMA and LiClO<sub>4</sub> stirred for 6 hrs separately at room temperature, and then both the solutions were stirred for 24 hrs and poured in a Teflon Petri dish. The sample was

removed at room temperature after 24 hrs. For complete removal of solvent the samples were vacuum dried at 50°C for another 12 hrs.

X-ray diffraction (XRD) was carried out with the help of a Shimadzu diffractometer operating at 40 kV and 30 mA for Cu K $\alpha$  radiation ( $\lambda=0.154$  nm). The scan rate was 2°C/min under the diffraction angle  $2\theta$  in the range of  $2\theta = 10^\circ - 80^\circ$ . Further differential scanning calorimeter (DSC) measurements are carried out using SII EXSTAR 6000 instrument for which 1-2 mg of the sample is used. The samples are heated at the rate 20°C/min over a temperature range of 30°C -150°C in a heating cycle for polymer blends. The conductivity studies are carried out using Thermo scientific model Nicolet iS5, iD5 ATR connected with a computer for data acquisition over a frequency range between 5 Hz and 1MHz.

### III. RESULT AND DISCUSSION

#### 3.1 Morphological properties:

The size and shape of the particles of polymer blend film of PEO/PMMA with 5 wt% of LiClO $_4$  was analyzed using SEM and are given in Fig 1 (a)&(b). The diameters of particles were measured to obtain the particle size. The various sizes of some of the particles 37.45 $\mu$ m, 58.9 $\mu$ m, 59.5 $\mu$ m, 74.2 $\mu$ m, 98.2 $\mu$ m, it also observed that the particles formed mostly spherical in shape which can be seen from SEM image.

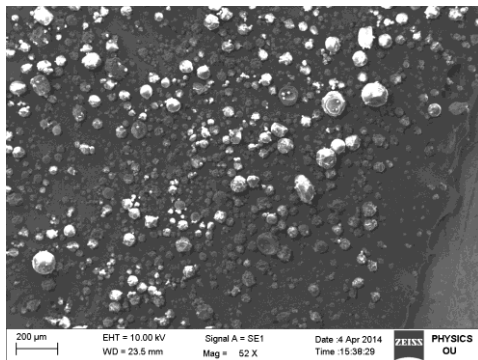


Fig 1(a): SEM Image of the PEO/PMMA/LiClO $_4$  (2wt %)

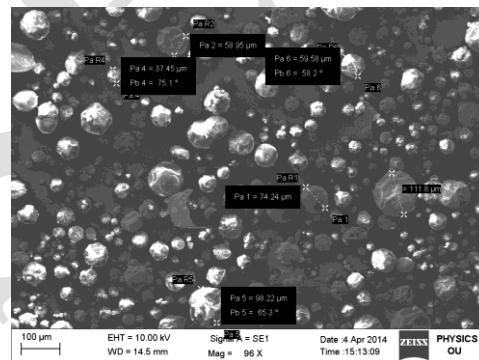


Fig 1(b): PEO/PMMA/LiClO $_4$  (5wt %)

#### 3.2 Structural properties:

The XRD pattern of pure PEO is shown in Fig 2(a) which contains two strong crystalline peaks at 20° and 24.07°. The higher intensity of these diffraction lines is suggesting that the PEO is intrinsically crystalline polymer with high crystallinity [12]. The intensity of these peaks of crystalline PEO decreases with PMMA content as shown in figures 2(c) It is evident from Fig 2(d) that LiClO $_4$  content films show an amorphous nature, and the sharp crystalline peaks correspond to the LiClO $_4$  salt were found to be absent in the complexes and there is no additional peaks observed in the complex which confirmed the complexation of lithium salt with PEO- PMMA blend electrolyte [13-14]. This amorphous nature may lead to higher ionic conductivity which is generally observed in amorphous polymer electrolytes with flexible backbone [15]

#### 3.3 Thermal properties:

In present work the DSC measurements are carried out in order to investigate the effect of varying weight percentage of LiClO $_4$  on thermal characteristic of polymer blends. As observed from Fig. 1(a) to 1(c), the peak width increases gradually on the addition of the filler. It is due to the formation of amorphous phase with in space charge layer between blend and LiClO $_4$ . Similar observations were made by sultana *et al* [16] and sumanthipala *et al* [17] in TII-Al $_2$ O $_3$  and PEO-LiBOB-CP-SZ composite system respectively, and observed that the broadening of melting peak is due to the increase of amorphous nature of the sample.

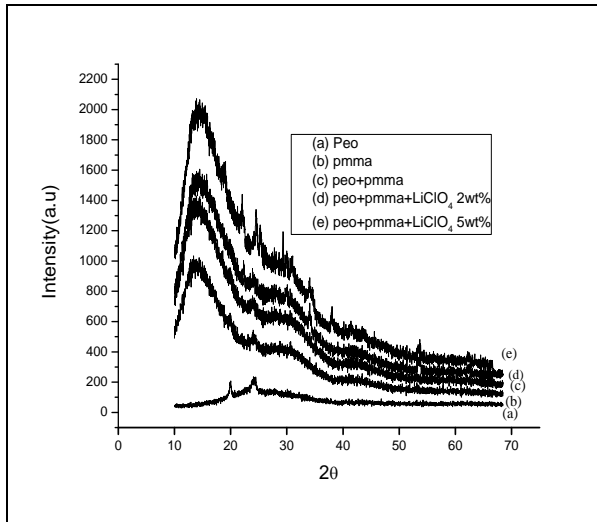


Fig 2: X-ray diffraction patterns of PEO, PEO/PMMA, and PEO/PMMA/LiClO<sub>4</sub> ternary mixture at different wt% of LiClO<sub>4</sub>

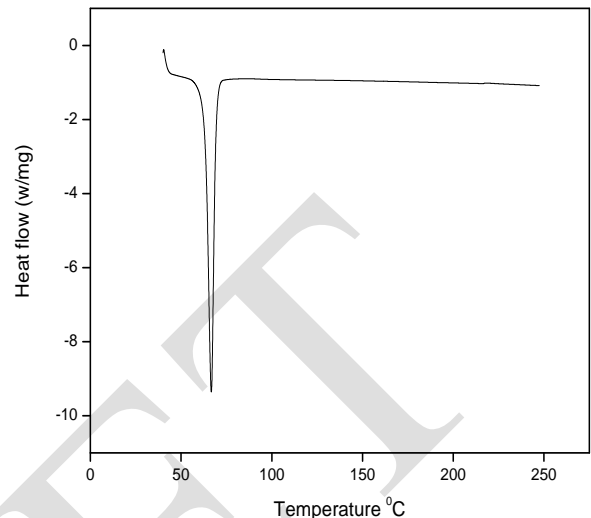


Fig 3(a) DSC thermogram for (a) PEO

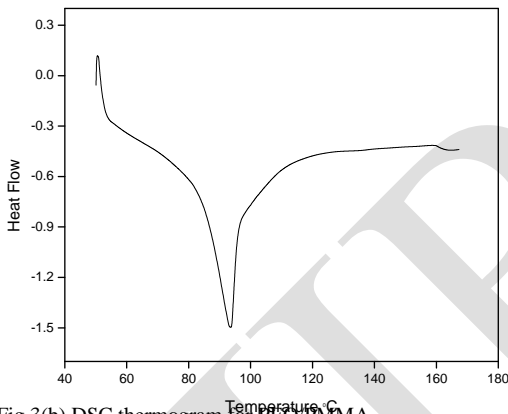


Fig 3(b) DSC thermogram for PEO/PMMA

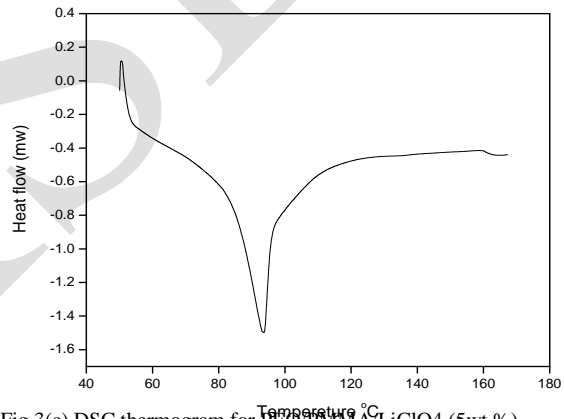


Fig 3(c) DSC thermogram for PEO/PMMA/LiClO<sub>4</sub> (5wt %).

### 3.4 Conductivity studies:

The dielectric properties of PMMA/PEO films and its composites with LiClO<sub>4</sub> are studied as a function of frequency at room temperature. The values of dielectric constants are obtained from the measured values of capacitances using eqn (1).

$$\epsilon' = Cd / \epsilon_0 A \dots\dots\dots(1)$$

Further, from the values of dielectric constants, dielectric loss and a.c conductivity ( $\sigma_{ac}$ ) are calculated using the eqns (2) & (3) respectively, which are given below.

$$\epsilon'' = \epsilon' \tan(\delta) \dots\dots\dots (2)$$

$$\sigma_{ac} = \omega \epsilon_0 \epsilon' \epsilon'' \dots\dots\dots (3)$$

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Where 'C' is capacitance of the dielectric material,  $d$  is thickness of the film,  $A$  is area of the film and  $\epsilon_0$  is the permittivity of free space.

The dielectric loss of blends films with 2, 3, 4 and 5 weight percentages of  $\text{LiClO}_4$  are obtained as functions of frequency using Equation (2) and are given in Fig 4(a). The dielectric loss of these polymer blend films decrease at low frequency range 5 Hz to 2 KHz and afterwards it remains constant at higher frequency range. Further as the weight percentage of  $\text{LiClO}_4$  increases dielectric loss of polymer blend films decreases.

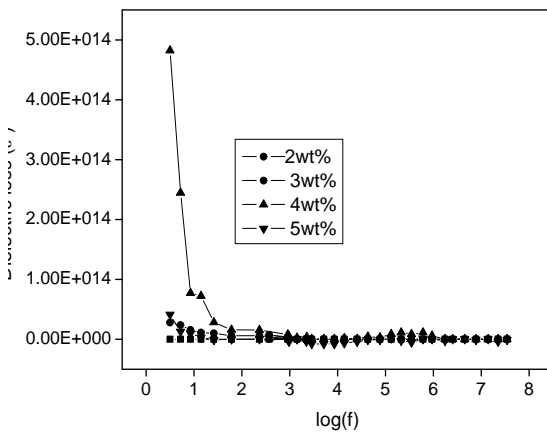


Fig 4(a) shows dielectric loss

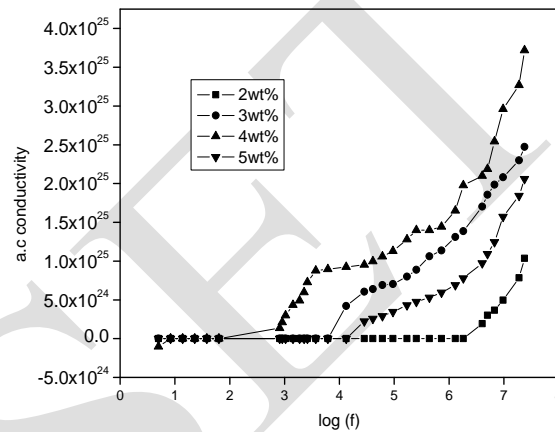


Fig 4(b) shows a.c conductivity of polymer blend with different wt% of  $\text{LiClO}_4$

The frequency-dependent a. c. electrical conductivities of PEO/PMMA/ $\text{LiClO}_4$  obtained at room temperature are shown in Fig 4(b). The polymer blend film shows similar behavior up to 104 Hz, i.e. there is no significant variation in the conductivity with frequency over this range. Further as the frequency is increased conductivity increases. It is important note that, the conductivity of all the polymer blends is significantly higher at higher concentration of  $\text{LiClO}_4$ . This may be understood that a polymer chain in the amorphous phase is more flexible resulting in an increased segmental motion of the polymer, which facilitates higher mobility of ions [18].

## IV. CONCLUSION

The XRD characterization reveals that the crystallinity of the PEO reduced with the addition of PMMA and  $\text{LiClO}_4$ . The amorphous phase is responsible for the conduction of ions through the PEO/PMMA blend matrix, which is revealed by DSC analysis. The conductivity measurements showed that as the ratio of filler increases the ionic conductivity also increases. The observed higher ionic conductivity in the polymer blends with  $\text{LiClO}_4$  is due to the creation of more conducting pathways resulting in increased chain flexibility and carrier concentration.

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