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Development and Characterization of Poly-ε-Caprolactone-Based Polymer Electrolyte for Lithium Rechargeable Battery

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A biodegradable polymer electrolyte based on Poly-ε-caprolactone (PCL) with various level of concentrations of Lithium salt and plasticizer have been synthesized under both the ambient and vacuum environments. The ionic conductivity, morphology, topology and structural properties are examined using EIS, SEM and XRD respectively. Conductivity as high as 3.48E^{-04} Scm^{-1} and 4.99E^{-04} Scm^{-1} are obtained for the ambient and vacuum environment respectively. Ionic mobility is improved by increasing the amorphousity content of the polymer and degree of salt dissociation with plasticizer. Ionic conductivity is further enhanced with the addition Li salt to increase the free ions concentration. Ionic conductivity measurements are further supported by the XRD data which reveal that sample with higher amorphous content tends to show higher conductivity. The dielectric relaxation study in terms of characteristic of the structural molecular interaction and ionic transportation properties are also carried out. Both of the conductivity and XRD results are further verified by SEM images.

Keywords: Polymer Electrolyte; Impedance Spectroscopy; Biodegradation; Poly-ε-caprolactone; Lithium Triflate.

1. INTRODUCTION

The ongoing efforts to replace liquid electrolyte have led to the development of polymer electrolyte battery. Polymer electrolyte battery is not only well-known for its safety features but for its high power density, flexibility, plasticity of size and shape [1, 2]. In addition, it also play a key role as binder for the electrode as it simplifies the fabrication process of battery cell. It is anticipated that the reduction in power consumption of electronics devices, and a thin film like solid polymer electrolyte will be adequate to power these devices. However, with the advancement of technology, the hunger for higher power density in portable electronics devices such as hand-phone has led to the requirement of high power consumption as a result of increasing functionality. Many strategies and approaches have been deployed to increase the ionic conductivity such as plasticizing the polymer electrolyte with small organic molecules e.g.s ethylene carbonate (EC) or dimethyl carbonate (DMC) which has high dielectric constant and low vapor pressure to address such need. However, minimal research on biodegradable polymer electrolyte is reported for the past decade. One of the primary concerns that discourage research in polymer electrolyte is believed to be due to the environmental impact it would bring if polymer electrolytes are used in large amounts [3]. To address such concern, research on developing biodegradable polymer electrolyte using “ecomaterials” have become increasingly important with the aim to reduce the environmental impact [4].

In this paper, an effort has been made to study the potential of using a biodegradable polymer as an electrolyte to replace the use of conventional liquid type and polymer electrolyte which are deemed harmful to the environment. PCL was chosen as host material for its noticeable natural degradation and mechanical strength as it only able to dissolve in organic solvent [5, 6, 7]. The biodegradable polymer system under study here composed of PCL as host polymer and Ethylene Carbonate (EC) as plasticizer containing Lithium Triflate ($LiCF_3SO_3$). The characterisation results on the biodegradable polymer system in this study such as EIS, SEM and XRD are analyzed and discussed in terms of ionic conductivity, dielectric relaxation and morphology of the polymer electrolyte.

2. EXPERIMENTAL

2.1 Samples preparation

The biodegradable polymer electrolyte samples were prepared using solution casting technique. The solution contained mixture of Lithium Triflate ($LiCF_3SO_3$), Poly-ε-caprolactone (PCL), and Ethylene Carbonate (EC) which were dissolved in Tetrahydrofuran solvent (THF) with an optimal composition from each of the components to obtain maximum conductivity. The mixture of the samples was stirred using magnetic stirrer until a homogenous solution was attained. The resulted homogenous solution was transferred into a petri dish and stored in two different environments (high vacuum and ambient) and left to dry by solvent evaporation until a thin film was formed.

2.2 Characterizations

Electrochemical experiments were carried out to measure the impedance of the electrolyte thin film samples. HIOKI 3531, an a.c impedance spectroscopy interfaced with a computer was used to perform the impedance measurement for each sample with frequency ranging from 50Hz to 1 MHz. The electrolytes samples were sandwiched between the stainless steel discs with an area of $1.0cm^2$ to simulate an ion blocking electrodes. The ionic conductivity can then be determined from the bulk resistance, (Rb) obtained in cole-cole plot by using the following equation:

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

Where σ = ionic conductivity;

t = thickness of the sample;

A= surface area of the sample;

Moreover, complex impedance, dielectric constant, dielectric loss and loss tangent were also presented and their relationship can be obtained from Macdonald [8]. Other than impedance measurement, scanning electron microscope (SEM) and X-ray diffraction spectroscopy (XRD) were used to study the surface morphology and crystallinity of the thin film sample prepared to support the conductivity result studied.

3. RESULTS AND DISCUSSIONS:

3.1 Ionic conductivity

The dependency of ionic conductivity on Lithium Triflate concentration was analyzed by examining the log σ versus lithium Triflate and the EC plots from various compositions. The room temperature of the ionic conductivity of pure PCL film, (PCL+35%wt EC) at vacuum and (PCL+30wt% EC) ambient environment were $3.67E^{-10}$ Scm^{-1}, $2.97E^{-09}$ Scm^{-1} and $9.07E^{-10}$ Scm^{-1} respectively. PCL as a host was expected to have very low conductivity or act as an insulator without lithium salt to provide free carrier ions for conductivity. It is observed that the ionic conductivity started to increase when more than 20% wt of Triflate ($LiCF_3SO_3$) was inserted in to pure PCL as illustrated in Fig 1 (a) and Fig 1 (b) respectively. The highest ionic conductivity obtained in the (PCL+ $LiCF_3SO_3$) system at room temperature were 8.91×10^{-5} Scm^{-1} (vacuum) and 1.17×10^{-4} Scm^{-1} (ambient) respectively. The ionic conductivity increased with the increase of Lithium Triflate concentration as the number free ions increases [9]. However conductivity started to decrease once the ionic conductivity of the polymer electrolyte reached its saturation level. This phenomenon existed due to high number of free ions in the sample getting too close to each other and that increased the possibility of ion pairs, triplet or higher ion aggregations which in turn reduced the overall number of effective charge carriers and ion mobility as reported by MacCallum [10].

By combining the Lithium Triflate and plasticizer (EC) into both the systems, ionic conductivity was found to be further enhanced to maximum conductivity of $3.48E^{-04}$ Scm^{-1} (vacuum) and $4.99E^{-04}$ Scm^{-1} (ambient) as shown in Fig 1 (c) and Fig 1 (d) respectively. The main function of the EC is to reduce the viscosity of the electrolyte and help to improve the lithium ion dissociation thus increasing the number of free ionic carrier for conductivity (Macfarlane et. al, 1995) [11]. At high Lithium Triflate concentration, ionic conductivity no longer dependent on the number of free ionic and dominantly influenced by the mobility of the free ionic carriers that is directly proportional to the viscosity of the electrolyte. Similar observation was also reported by Kumudu Pererav and H.P Chen. [12, 13]

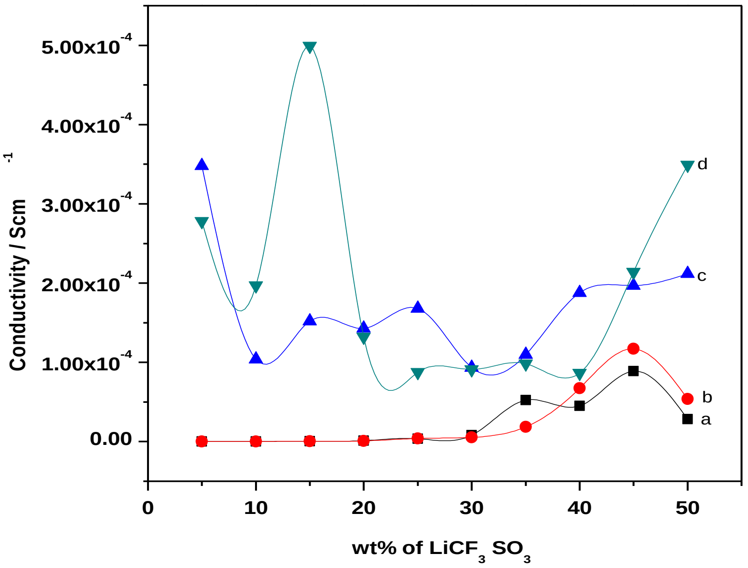
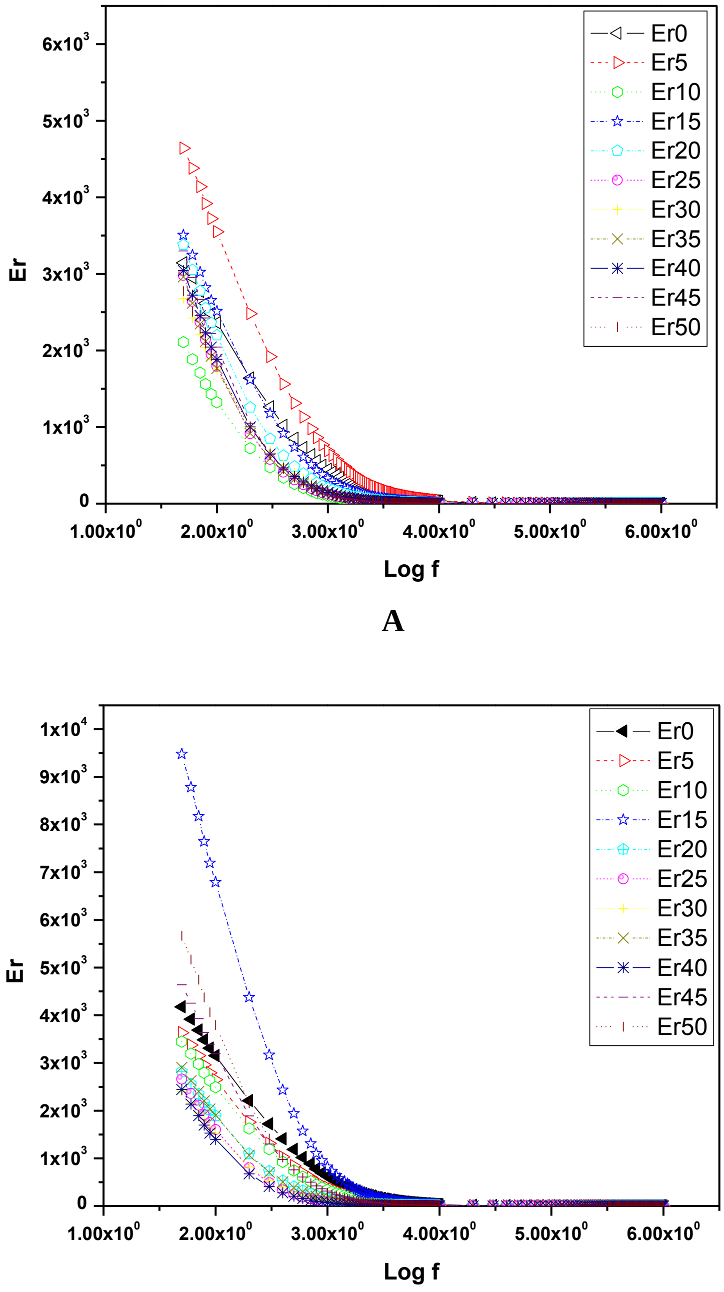


Figure 1. Ionic conductivity versus Lithium salt content for the: (a) (PCL+ $LiCF_3SO_3$) vacuum system, (b) (PCL+ $LiCF_3SO_3$) ambient system, (c) (PCL+ EC +$LiCF_3SO_3$) vacuum system, (d) (PCL+ EC + $LiCF_3SO_3$) ambient system

3.2 Complex permittivity

Dielectric constant (ε_r) is a measure of reduction of coulomb interaction between the ion pairs in the polymer electrolyte blends. This dielectric property provided valuable information such as characteristic of the ionic/molecular interaction of the polymer electrolyte and the understanding of ion transport behavior as well. In all the cases, the increase in dielectric constant implied the increase in the number of ions. These observations correlated well with the higher conductivity attained depicted in Fig 2 (a) and Fig 2 (b) when plasticizer (EC) and Lithium Triflate were inserted to improve the conductivity. From the figures, due to charge accumulation at the electrode–electrolyte interface and polarization effects, the ε_r value increased sharply at the lower frequency region. However, at higher frequency region, a decrease of ε_r in value was observed. This could be attributed to the periodic reversal of the electric field occured so rapidly that there was no significant diffusion in the direction of the electric field [14]. It was observed that the addition of plasticizer and Lithium Triflate increased the ε_r value in lower frequency region which resulted in more localized charge carriers with mobile ions lead to enhancement in dielectric constant [14, 15, 16]. This was also in agreement with Wintersgill and Fontanella [17] and Gray [18] investigations concerning the permittivity of Lithium Triflate in polymer systems.



A

B

Figure 2. A Dielectric constant plot for the PCL + 35wt. % EC +5wt. % $LiCF_3SO_3$ vacuum environment. **B** Dielectric constant plot for the PCL + 30wt. % EC + 15wt.% $LiCF_3SO_3$ ambient environment.

Fig 3 (a) and Fig 3 (b) show the variation of tangent loss with the best composition of PCL/EC/$LiCF_3SO_3$ at different frequencies. The tangent loss (tan δ) spectra was characterized by peak appearing at a characteristic frequency for both samples fabricated in two different environments showing the presence of dipoles relaxation in all of the samples. The tangent loss peak shifted to higher frequency with a higher ionic conductivity. It was evidenced that, good combination of EC and Lithium Triflate increased the amorphosity of the materials with optimum amount of free ionic charge carriers thereby increased the segmental motion of polymer and enhanced the ion transport properties as the peak shifted to higher frequency side. A similar finding was reported by S.L Agrawal et. al whereby the additional of EC can enhance the amorphous level of polymer electrolyte thus produce relatively fast segmental motion coupled with mobile ion in the tan δ versus frequency curve [16].

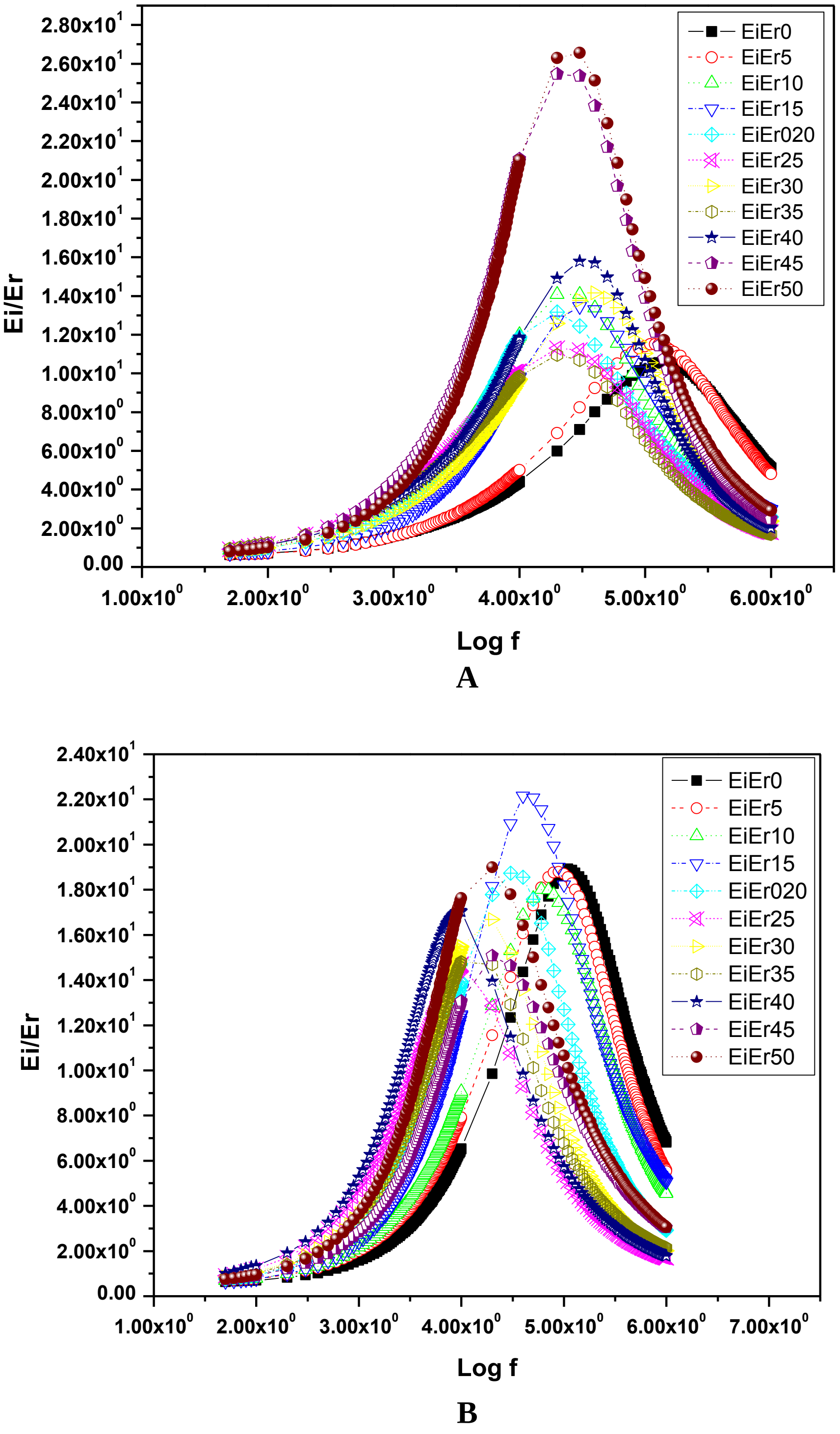
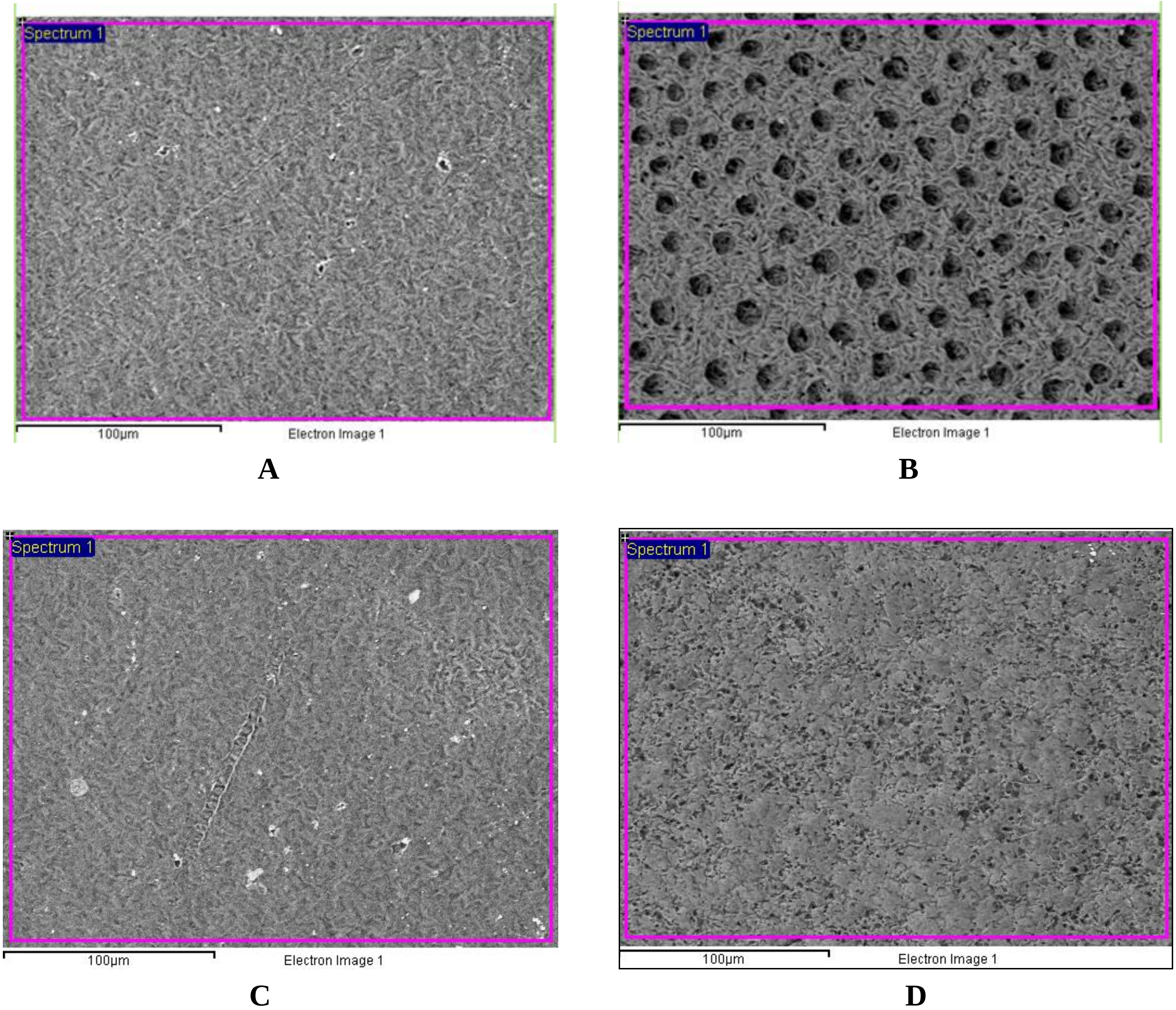


Figure 3. A) Tangent plot for the PCL + 35wt. % EC +5wt. % $LiCF_3SO_3$ vacuum environment. **B)** Dielectric constant plot for the PCL + 30wt. % EC + 15wt.% $LiCF_3SO_3$ ambient environment.

3.3 SEM & XRD analysis

All the samples were analyzed using scanning electron microscope (SEM) to study the topology and morphology of the polymer electrolyte fabricated. Fig. 4 a-d show the SEM images of polymer electrolyte at different blending of composition and ratio respectively. Higher pores or craters observed in the micrograph for the sample fabricated in the ambient environment were due to rapid evaporation of solvent (THF) as shown in Fig 4 (a) and Fig 4 (b). The difference of pore sizes was mainly due to the difference in the driving force for phase separation [19, 20]. The combination of $LiCF_3SO_3$ and EC added into the polymer electrolytes found smoothens and increased the amorphosity of the polymer electrolyte as seen in figure Fig 4 (b) and Fig 4 (c). Moreover, "Spherulite" form of surface observed with the insertion of Lithium Triflate ($LiCF_3SO_3$) indicated the interaction between Lithium salts, polymer host and plasticizer.



A **B**

C **D**

Figure 4. A) SEM image for pure PCL fabricated in vacuum environment. **B)** SEM image for pure PCL fabricated in ambient environment **C)** SEM image for PCL + 30wt. % EC + 15wt. % $LiCF_3SO_3$ **D)** SEM image for PCL + 35wt. % EC +5wt. % $LiCF_3SO_3$

Fig. 5.1 and Fig. 5.2 show the XRD pattern for pure PCL film and from the highest conducting film from (PCL+ $LiCF_3SO_3$), (PCL+EC) and (PCL+ EC+ $LiCF_3SO_3$) in both vacuum and ambient environment. The XRD pattern in Fig. 5 (a) for pure PCL film illustrated that the structure of the thin film was a semicrystalline with the peak at 21.4° and 23.6°, which correspond to the orthorhombic planes (110 and 200) of PCL [21]. The XRD pattern in Fig. 5.1 b-d and Fig. 5.2 b-d demonstrated that all the peaks pertaining to Lithium Triflate and EC were not present in the complexes.

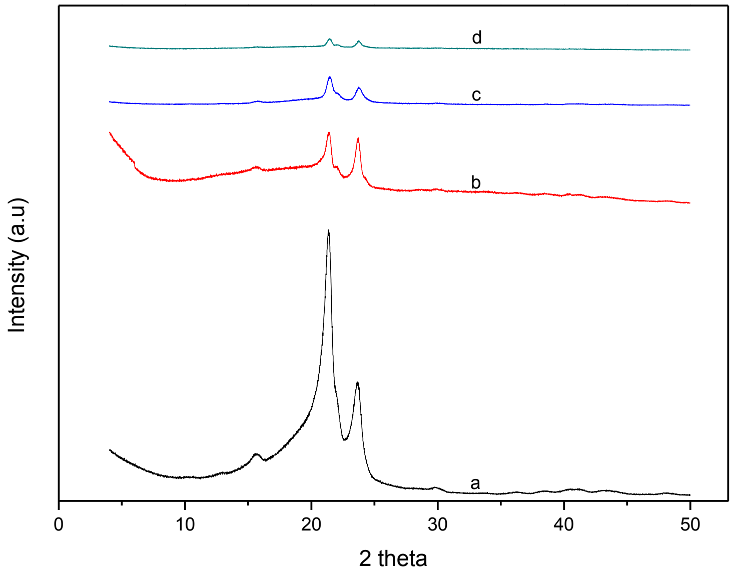


Figure 5.1 (a): XRD pattern of the (a) pure PCL, (b) PCL+45wt.% $LiCF_3SO_3$, (c) PCL+ 35wt. % EC, (d) PCL+ 35wt. % EC +5wt.% $LiCF_3SO_3$. (vacuum environment).

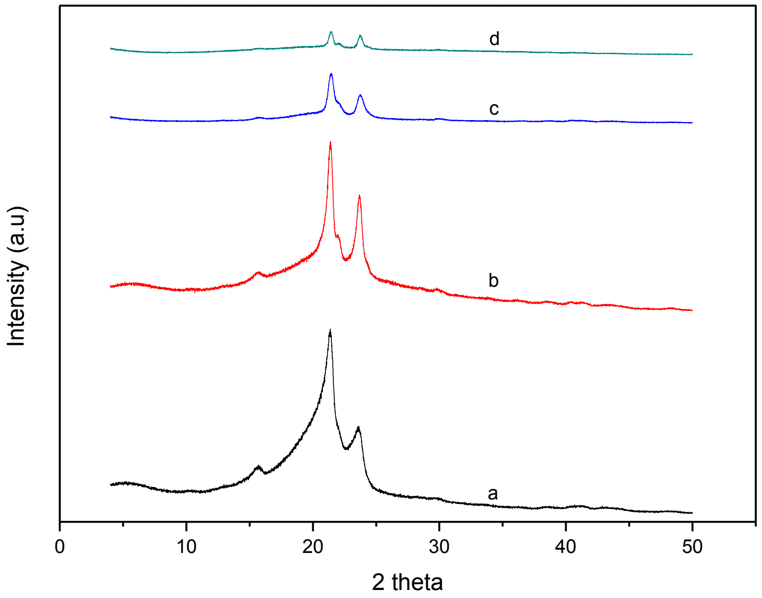


Figure 5.2 (a): XRD pattern of the (a) pure PCL, (b) PCL+45wt.% $LiCF_3SO_3$, (c) PCL+ 30wt. % EC, (d) PCL + 15wt. % EC +45wt.% $LiCF_3SO_3$. (ambient environment).

This indicated that there was a complete dissolution and interaction of the Lithium Triflate and EC in the polymer matrix. Significant reductions in diffraction peak intensity were found in the complexes with mixture of EC and Lithium Triflate. The decrement of the diffraction peak intensity with the additional Lithium Triflate and EC illustrated the transition process from semicrystalline structure to amorphous structure. Similar observations were reported by Berthier et al. (2001) where ionic conductivity level in polymer electrolyte was correlated to the amorphous phase of the samples [22]. This result further verified the ionic all the studies above.

4. CONCLUSION

The development of environmental friendly polymer electrolyte fostered using PCL complexes with Lithium Triflate and Ethylene Carbonate had been successfully demonstrated. Low ionic conductivity value was found in PCL without the presence of Lithium Triflate. With the introduction of Lithium Triflate into PCL, conductivity was dramatically enhanced to $8.91\text{x}10^{-5}$ Scm^{-1} (vacuum) and $1.17\text{x}10^{-4}$ Scm^{-1} (ambient) respectively. Maximum ionic conductivity of 3.48E^{-04} Scm^{-1} and 4.990E^{-04} Scm^{-1} had been archived with good combination of Lithium Triflate and EC in the PCL/EC/$LiCF_3SO_3$ system for both ambient and vacuum environment respectively. These findings were further supported by the XRD and SEM analysis. It was concluded that that higher porosity and amorphousity of the sample can help to increase the ion transference numbers hence, higher conductivity could be attained.

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