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Conductivity and Microstructure Study of PLA-Based Polymer Electrolyte Salted With Lithium Perchloride, $LiClO_4$

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A series of polylactide PLA based solid polymer electrolytes have been prepared using a solution cast technique. The ethylene carbonate (EC) is chosen as a plasticizer, SiO_2 was implemented as ceramic filler and the lithium perchlorate salt ($LiClO_4$) as a main ions carrier to the polymer host systems. The conductivity behaviours of the samples prepared were studied by ac impedance spectroscopy (EIS), X-Ray Diffraction (XRD) and electron microscope technique (SEM). From the results obtained from various scientific analyses, it was proven that 20 wt% of $LiClO_4$ added into the PLA–EC system shows best performance with the highest conductivity value of 1.44×10^{-6} S cm^{-1}. The conductivity is further enhanced to 1.29×10^{-5} S cm^{-1} with the addition of 2 wt % of SiO_2. The studies showed that the salt is helped to increase the number of charge carrier and provided free ions for conduction whereas ceramics fillers are capable of providing an extra conduction channels that further enhanced the conduction factor of the polymer electrolyte. Ionic conductivity increased with respect to the enhancement of the charge carried and filler, however excessive amount of these additives caused the conductivity to decrease. The results are further proven and supported by XRD and SEM studies.

Keywords: PLA, XRD, Impedance, lithium perchlorate, polymer electrolyte

1. INTRODUCTION

An electrolyte is an essential component of an electrochemical cell, be it a battery or fuel cell for producing electrical energy. Electrolyte can also be defined as electrically conductive substance that containing free ion. Polymer can be referred as the conducting macromolecules having high molar mass composed of a large number of repeating structural units. These repeating units are connected to each other by covalent chemical bonding to form a long chain. The term “polymer” is derived from the

Greek poly, meaning “many” and mer means “part”. Normally the electrolytes are solution of acids, bases or salts. Polymer electrolyte is flexible and lightweight, perform better than liquid electrolyte. It has wide range of electrochemical windows. The main drawback from polymer electrolyte is their low ionic conductivity in low temperature [1].

SPE is different from gel and liquid electrolyte. It is established by a relatively high constant polymer such as poly (methyl methacrylate) (PMMA), polyacrylonitrile (PAN), polyethylene oxide (PEO), polyvinyl alcohol (PVA) and a salt with low lattice energy. The mechanical strength and conductivity of the SPE can be increased by plasticizer and filler. Another famous electrolyte is the liquid electrolyte which is applied in lithium battery configured anode (lithium metal) and cathode (lithium metal oxide). The use of lithium metal can give high specific energy batteries but they have a major problem related to the chemical surface products that develop on the lithium anode that may developed an outgassing effect causes high pressure inside the battery. By the use of SPE can solve these problems. The SPE rechargeable lithium batteries are expected to surpass the performance of conventional liquid electrolyte systems. The large-scale production of solid-state batteries could benefit from well-established technologies developed in the polymer industry. The key component of the lithium polymer battery is the electrolyte. High ionic conductivity, good mechanical properties and compatibility with the electrode materials are the appropriate choice of this component [2].

Biodegradable polymers have aroused a lot of interest in view of its applications in the industrial and biomedical sectors [3].Using biodegradable polymers from renewable sources can help reduce certain environmental problems and also increase the applications of biodegradable polymer electrolytes. Pradeep and Shikha [4] appraised the recent developments in the area of polymer electrolytes using aqueous and non-aqueous based natural polymers for developing a cheaper, ecofriendly, biodegradable, and widely used electrolytes as a substitute for existing synthetic polymer electrolytes.

The mass production of polymer electrolyte will bring environmental impact due to some polymer is non-degradable[5,6]. The development of polymer electrolyte previously is mainly focus on synthetic polymer but now is being replaced by biodegradable polymer electrolyte. Some example biodegradable polymer such as starch and cellulose are commonly used. To solve this problem, research on developing biodegradable polymer electrolyte by using “ecomaterials” or environmental “conscious” material have become increasingly important with the aim to reduce the environmental impact [7]. Thus, the solution is to find a good combination of polymer electrolyte to yield high ionic conductivity, biodegradable and chemical stability as well as good mechanical strength.

Biodegradable polymers do possess some other outstanding criteria: 1) sustainable owing to its renewable nature that does not deplete as the petrochemical source, 2) cheap in cost since it is naturally occurring polymer and 3) biodegradable nature that makes it more environmental-friendly [8,9]. The selection of biodegradable polymer in the development of conducting medium needs a lot of consideration since it is highly crystalline in nature. The crystallinity of polymer is characterised by their degree of crystallinity which ranges from zero for a completely non-crystalline polymer to one for a theoretical completely crystalline polymer. Polymers with the degree of crystallinity approaching zero or one will be transparent, while polymers with intermediate degrees of crystallinity appears as opaque due to light scattering by crystalline or glassy regions. Thus for many polymers, reduced crystallinity may also be associated with increased transparency.

In this research, the main objective was to develop the novel electrolyte which using biodegradable polymer. Since the ionic conductivity for the biodegradable polymer is low, various effort such as adding salt, adding plasticizer and adding filler to improve the reliable and the usage of the battery. Various approaches are made in order to improve the ionic conductivity, dielectric constant, electrical and electrochemical as well as mechanical properties. In this research, the biodegradable polymer that is chosen is polylactide (PLA) with lithium perchlorate ($LiClO_4$) as dopant salt upon addition of ethylene carbonate (EC) as plasticizer, silica (SiO_2) as filler and Tetrafuran (THF) as solvent. This project was designed to explore the knowledge of rheological properties of the biodegradable polymer electrolytes. The morphological of biodegradable polymer electrolytes were analysed by scanning electron microscopy (SEM), whereas the structural manners of polymer blend electrolytes were considered by means of X–ray diffractor (XRD).

2. EXPERIMENTAL

2.1. Sample preparation

All the polymer electrolytes were prepared by solution casting technique. There are four biodegradable polymer electrolytes systems. The quantity of materials added was expressed as weight percent (wt %). Appropriate amounts of materials were dissolved in THF. The solution was then stirred continuously for 24 hours on a hot plate (without heating) at room temperature to obtain a homogenous mixture of polymer system at room temperature. After that, the solution was cast on a glass Petri dish and allowed to evaporate slowly inside a fume hood .The Petri dish is covered with aluminium foil to avoid any contaminations.

In this work, three types of polymer electrolyte systems were prepared. The first system consists of pure PLA system which acts as reference and PLA system plasticized with different amount of EC that helps to soften the polymer matrix and the films formed are more flexible. The plasticized film is expected to have improved ionic conductivity even no lithium salts have being added into the system. In the second system, appropriate amount of lithium salts ($LiClO_4$) have been added into the predetermined composition from second system. The amount of host polymer is fixed but the amount of lithium salt is varies accordingly so that any changes of the conductivity values are mainly due to the addition of lithium salt. Finally, the third systems, SiO_2 are incorporated into the previous system that exhibits highest conductivity value with good mechanical strength.

2.2. X–Ray Diffraction (XRD)

The amorphous degree of polymer electrolytes was investigated using XRD. Siemens D 5000 diffractometer with Cu–Kα radiation (λ=1.54060 Å), over the range of 2θ=5–80° at ambient temperature were used to record the XRD pattern.

2.3. Scanning Electron Microscopy (SEM)

Using Leica' s SEM (model S440) at 10kV, the morphology of polymer samples at room temperature was studied. Insulator such as pure PLA was coated with a thin layer of gold to prevent electrostatic charging. The exchange of energy between the electrons and the sample cause emission of secondary electron and electromagnetic radiation that can be detected and generate SEM images.

2.4. Electrochemical Impedance spectroscopy (EIS)

By using HIOKI 3532–50 LCR HiTESTER over the frequency range of 50 Hz to 1 MHz, ionic conductivities of the samples could be determined. The samples were cut into a square shape of 1 cm^2 and fit into the size of electrodes. The samples were sandwiched between stainless steel blocking electrodes and clamped with screws.

The polymer electrolytes' ionic conductivity is determined by using the equation below.

$$\sigma = \frac{\ell}{R_b A}$$

where ℓ is the thickness (cm); R_b is the bulk resistance (Ω) and A is the recognized surface area (cm^2) of polymer electrolytes. The semicircle was fitted and this fitting was able to obtain R_b value. R_b was calculated from extrapolation of the semicircular region on Z real axis (Z'), as shown in figure 1 below. Besides, Z' and Z imaginary (Z'') axis must be in equal scale because the radius of a circle must be the same.

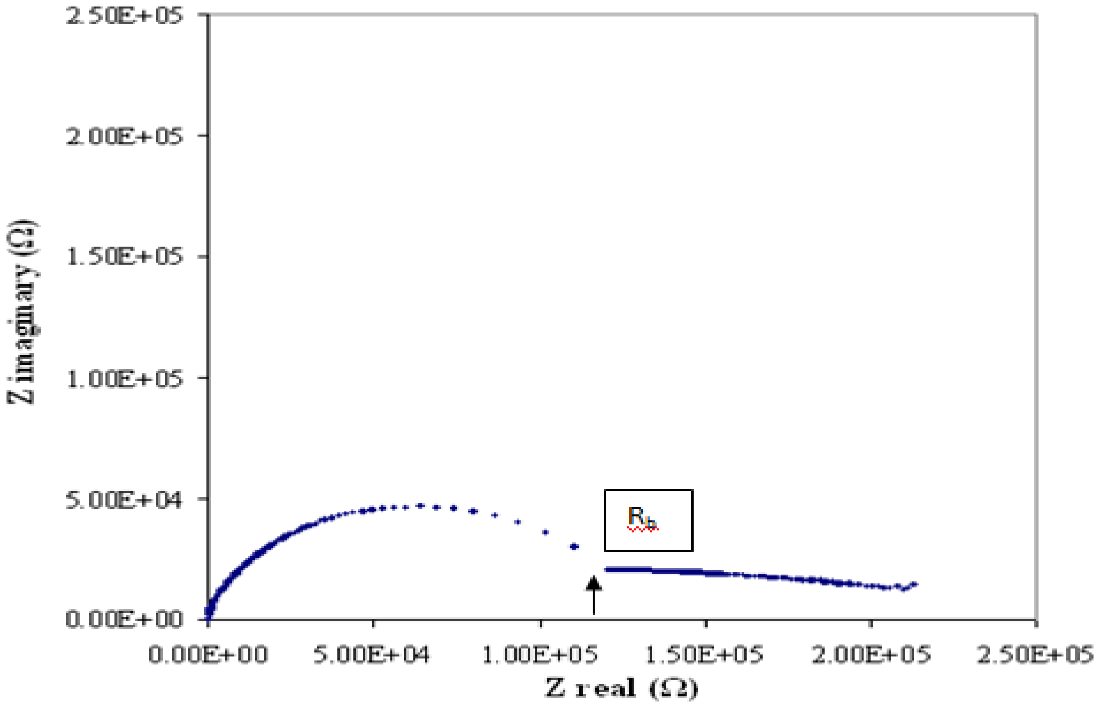


Figure 1. Typical Cole-Cole plot at ambient temperature

3. RESULT AND DISCUSSION

3.1. Ambient Temperature–Ionic Conductivity Studies

3.1.1 Conductivity of pure PLA

Figure 2 shows the ionic conductivity of the PLA with different EC weight percent at ambient temperature. The ionic conductivity of PLA film increase with EC weight percent, to the optimum level then it start to fluctuate. The ionic conductivity increase by the increase of EC is due to the long range coulombic forces leading to re–dissociation of solvated ion pairs. After that, large amount of free mobile charge will produced and they are ready for segmental transportation in electrolytic conduction. Thus, the ionic conductivity of PLA-EC film is increased due to segmental mobility of charge carrier is increased [10].

The 35 wt % of EC blended with PLA has 1.908 x 10 $^{-10}$ S cm^{-1} shows the highest ionic conductivity among other weight percent. This is because the EC at 35 wt % has reached the optimum level of mobile charger and cause it has highest ionic conductivity [10].Besides that, the addition of EC as plasticizer also decrease the ion pairing as they can effectively reduces the inter-ion Coulomb interactions, hence it will enhance the $LiClO_4$ added later to be contributes more in conductivity of polymer matrix. In general, all samples exhibit low ionic conductivity as there is no any salt or charge carrier being doped into the polymer yet.

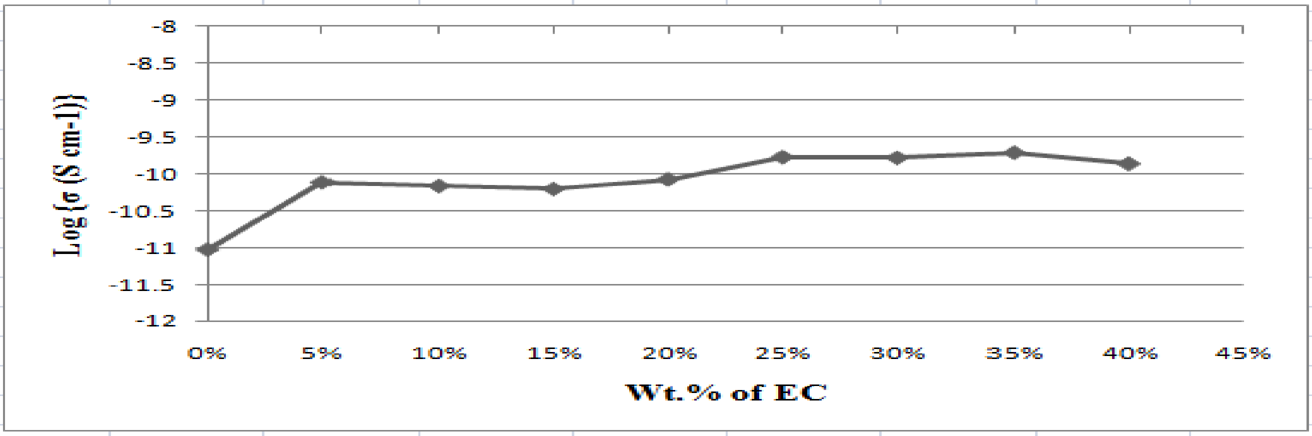


Figure 2. Variation of logarithm ionic conductivity as a function of Ethylene Carbonate (EC) weight percentage incorporated into PLA.

3.1.2. System II

The conductivity of polymer electrolyte is calculated from the semi-circle fit at the impedance plot. Figure 3 shows that the conductivity of PLA/EC/$LiClO_4$ solid polymer electrolyte increases through the addition of $LiClO_4$ and reaches highest conductivity at 20 wt % $LiClO_4$ (1.442 x 10^{-6} S cm^{-1}). The pure PLA is an insulator and it shows its conductivity is 9.46 x 10^{-12} S cm^{-1} from impedance plot.

This may be due to the increase in the number of free mobile ions [11]. These free mobile ions also increase the amorphous structure of the polymer through the favorable free volume and therefore the ion migration takes place easily. However, when more lithium salt was added, the conductivity decreases upon further additon of the amount of doping salt due to formation of neutral ion pairs [12] thus reducing the number density of mobile ions and hence the conductivity.

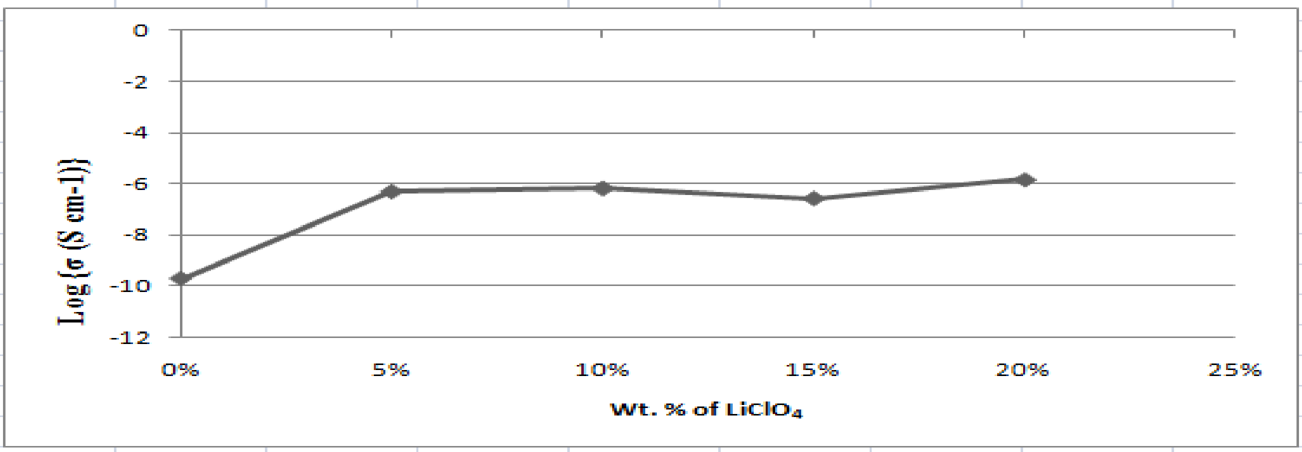


Figure 3. Variation of logarithm ionic conductivity as a function of Lithium Perchlorate ($LiClO_4$) weight percentage incorporated into PLA-EC.

3.1.3. System III

Conductivity data for composite gel polymer electrolytes containing different weight ratios of SiO_2 are presented in Figure 4. The ionic conductivity decreases with the addition of SiO_2 loading beyond 6 wt%. It is shown that ionic conductivity of polymer electrolyte has reached the highest value of 1.29 x 10^{-5} S cm^{-1} with 2 wt % SiO_2 in PLA-EC-$LiClO_4$. However, after this weight percent, the ionic conductivity of polymer electrolytes did not increases with increase of SiO_2 .It started to fall once the optimum concentration of SiO_2 (2 wt %) is reached.

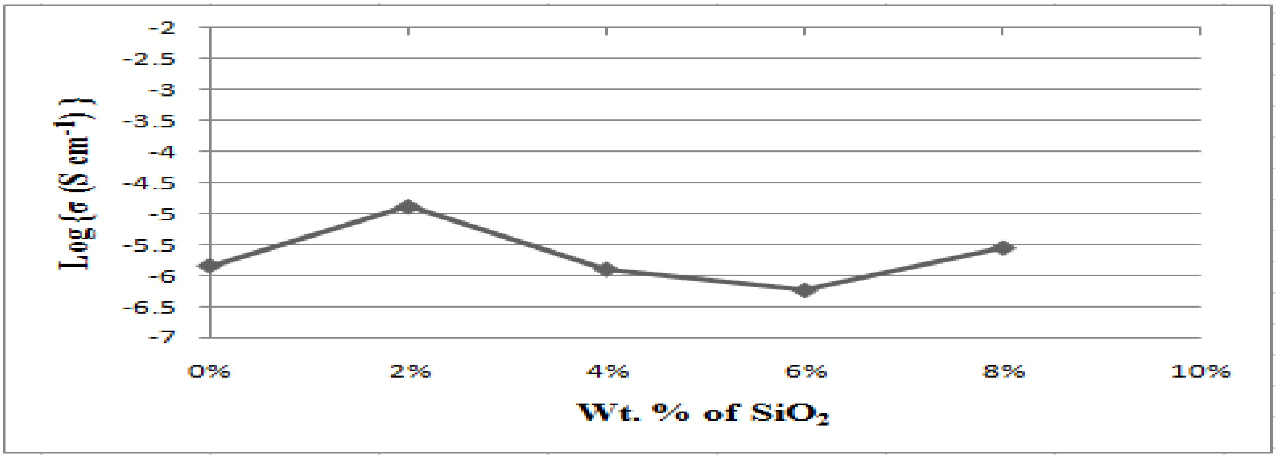


Figure 4. Variation of logarithm ionic conductivity as a function of Silicon dioxide (SiO_2) weight percentage incorporated into PLA-EC-$LiClO_4$.

Ionic conductivity has reached highest with 2 wt % of SiO_2. This is mainly attributed to higher degree of amorphous in the polymer system. It increases the defects concentration along the SiO_2 particles interface [13]. The ionic conductivity of polymer electrolyte does not increase with the increasing concentration of SiO_2 can be explained by a direct consequence of high concentration of SiO_2 which will lead to well defined crystalline regions.

3.1.4. Comparison of Different System

To have more understanding of ionic conductivity of polymer electrolyte, further investigate on the characteristic of salt towards PLA is shown. The graph above shows the different component of polymer electrolyte with their highest ionic conductivities. From the graph, it can be seen that the ionic conductivity when added EC is increases slightly only while for PLA+salt has show the increment of ionic conductivity dramatically due to salt can increase in the number of free mobile ions in polymer PLA[11]. The associated increase in the segmental flexibility of polymer chains would contribute to the conductivity enhancement. However, as shown in the graph, the conductivity enhancement is little compared with mixed with salt one. Thus, salt is main factor for the ionic conductivity in polymer electrolyte.

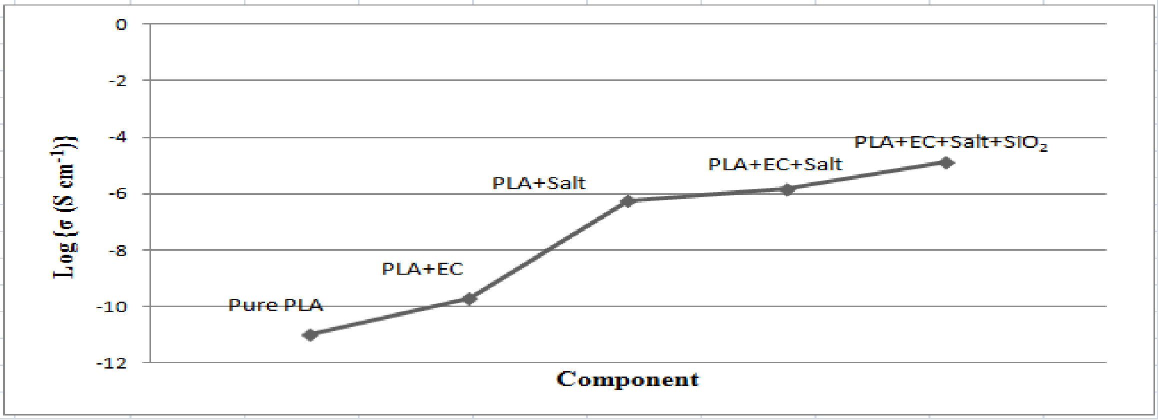
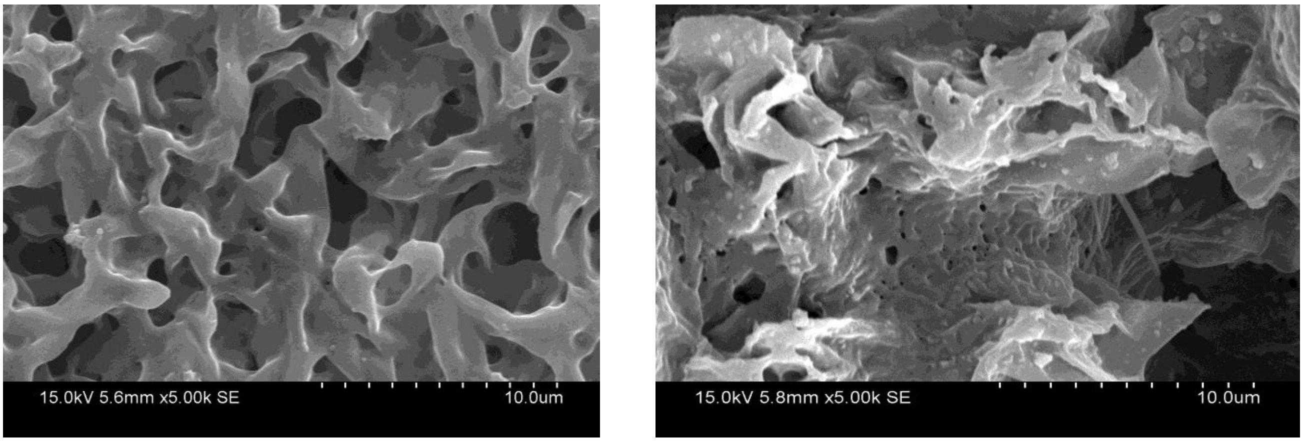


Figure 5. Comparison of different component of polymer electrolyte with their highest ionic conductivity in logarithmic.

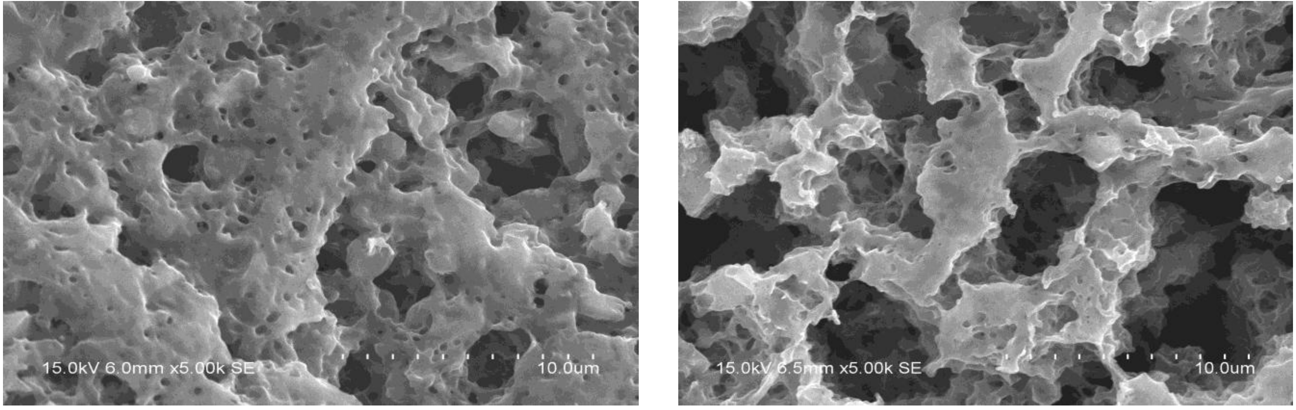
3.2. Scanning Electron Microscopy (SEM)

Figure 5 shows microstructures of selected SPEs in various blending systems .Results in SEM are quite congruent with its corresponding variation in ionic conductivity and activation energy. SEM has been suggested that morphological effects are responsible for increase in conductivity [14]. There are small craters are formed on pure PLA and PLA-EC and this is due to the rapid evaporation of THF solvent during the preparation of the thin film [15]. Pure PLA shows normal porous surface with uniform small pore size. When the film is mixed with 20 wt % of $LiClO_{4,}$ it appears become swollen as shows in figure 6(c). The addition of $LiClO_4$ tends to generates more compact and phase-separated matrix of polymer electrolyte. It also can be observed by comparing figure 6(b) that the pore size of

PLA-EC is much smaller and compact than PLA-EC with adulteration of $LiCLO_4$. This suggests the presence of structural reorganization of polymer chain and leads to Li^+ ion transportation in the polymer matrix [15]. Figures 6 (d) represent the SEM micrograph of the surface of different wt.% of SiO_2 in polymer complex system. The polymer thin film shows a very few and small pores of irregular shapes without addition with nanosized of SiO_2. After incorporation with 2 wt % of SiO_2, it showed a few obvious pores on the surface and starts to aggregate. The pore sizes on the surface increased and began to appear clearly on the surface. These aggregations are almost non-existent in the polymer complex system at 2 wt % of SiO_2. The highest ionic conductivity is also ascribed to the highest porosity.



(a) SEM for pure PLA. **(b)**SEM of PLA (65): EC(35)



(c) SEM of PLA/EC (80) : $LiClO_4$ (20) **(d)** SEM of PLA/EC/$LiClO_4$(98) : SiO_2 (2)

Figure 6. a) SEM for pure PLA b) SEM of PLA (65): EC(35) c) SEM of PLA/EC (80) : $LiClO_4$ (20) d) SEM of PLA/EC/$LiClO_4$ (98) : SiO_2 (2)

3.3 XRD

From Figure 4.7, a broad characteristic peak of pure PLA was obtained at angles of $2\theta = 17.02^\circ$ and at $2\theta = 29.90^\circ$ which reveals the amorphous phase of PLA .The broad peaks is called as amorphous hump and is a typical characteristic of amorphous materials. The amorphous nature results in a greater ionic diffusivity and high ionic conductivity, which can be obtained in amorphous polymers which possess flexible back bone. However, these characteristic peaks are decreased after addition of Ethylene Carbonate (EC). This implies that the addition of EC has disrupted the arrangement in the polymer backbone of PLA [16] . Further dilution of the crystalline phase could be noticed in Figure 4.7 upon the increase of wt % of the plasticizer EC, whereby broad and less intense peaks appear.

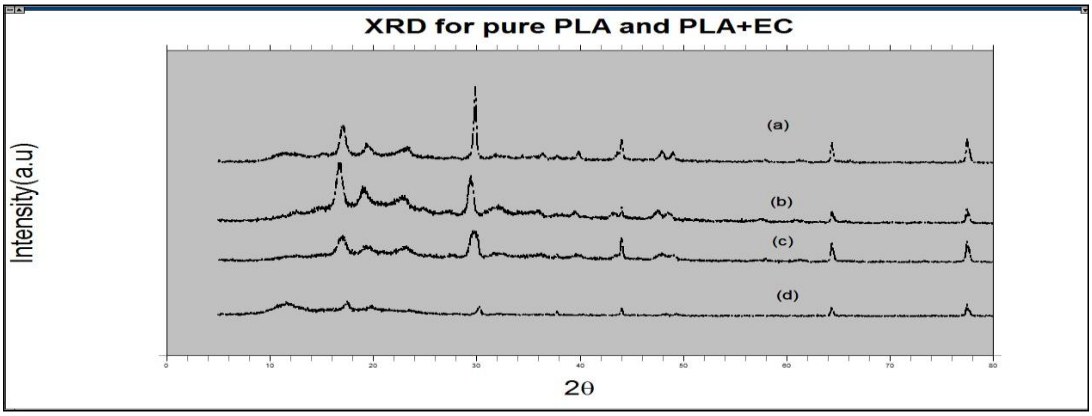


Figure 4.7. XRD for (a) pure PLA and PLA:EC (b) (95:5) , (c) (85:15) , (d) (65:35)

Figure 4.8 illustrates the sharp intense peaks at $2\theta = 16.74^{\circ}$, 29.52°, 44.00°, 64.36° and 77.44° and reveals the crystalline character of 10 wt % of LiClO$_4$. These crystalline peaks were disappeared when wt % of LiClO$_4$ increased PLA–EC polymer electrolytes. The absence of excess salt indicates that LiClO$_4$ is fully complexed with PLA and EC [17] .A complete dissolution in the polymer electrolytes leads to a complexation between PLA, EC and LiClO$_4$ [16]. Absence of these crystalline peaks in polymer electrolytes indicates that the electrolytes are in amorphous region. As shown in 4.21(a), the characteristic peaks of PLA–EC at $2\theta = 11.60^{\circ}$ and $2\theta = 17.50^{\circ}$ are shifted to 2θ angles of 16.74° and 29.52° for 10 wt % of LiClO$_4$, to 11.24° and 19.34° for 15 wt % of LiClO$_4$ and to 11.48° and 29.80° for 20 wt % of LiClO$_4$. This variation confirms the complexation between PLA–EC polymer film and LiClO$_4$ [18].

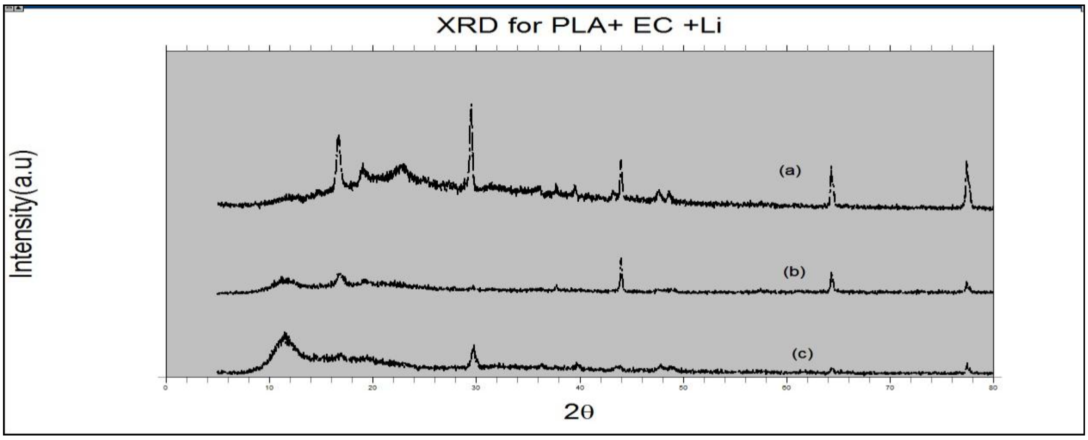


Figure 4.8. XRD for PLA-EC:Li (a) (90:10), (b) (85:15) and (c) (80:20).

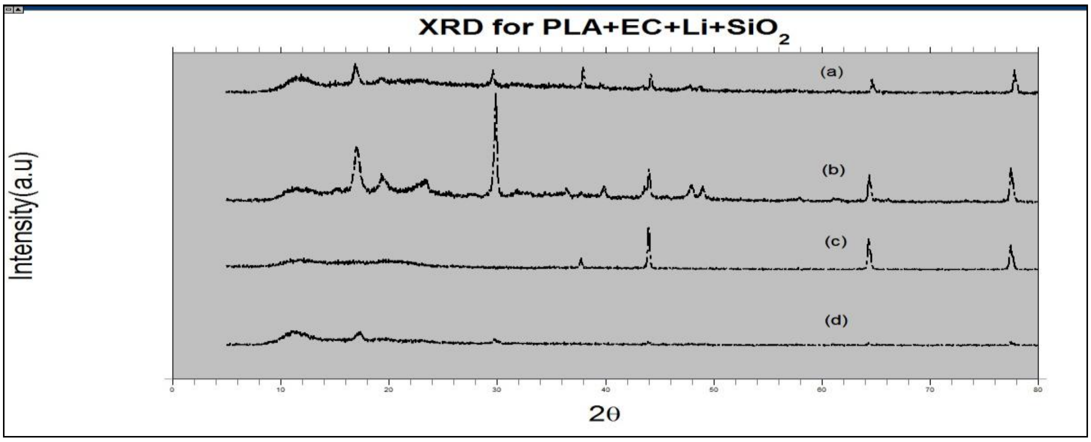


Figure 4.9. XRD for PLA-EC-Li:SiO_2 (a) (98:2), (b) (96:4) , (c) (94:6) and (d) (92:8)

Figure 4.9 shows the different wt % of SiO_2 in polymer complex system. On a closer inspection, it can be clearly noted that some of the peaks of pure PEO became relatively broader as well as less prominent after 2 wt % of SiO_2 dispersal. This is attributed to the increase in the degree of amorphousity in the SPE host. The degree of crystallization of polymer film decreases with the increasing of the amount of filler nanoparticles filled in. Maybe the interaction between the Lewis acid groups –OH on the surface of filler nanoparticles and the basic groups F atoms of polymer chains hinders the motion of polymer segments so the degree of crystallization for polymer film decreases [19].The nano-sized ceramic filler, due to its large surface area, prevents polymer chain re-organization, which results in “locking in” at ambient temperatures, a high degree of disorder characteristic of the amorphous phase, which in turn favors high ionic transport [19].

4. CONCLUSION

A solid polymer electrolytes based on PLA–EC–$LiClO_4$–SiO_2 complexes have been synthesized successfully by solution casting method. The incorporation of $LiClO_4$ salt, EC plasticizer and SiO_2 nano filler has led to significantly enhanced ionic conductivities. The composition PLA–EC–$LiClO_4$–2 wt %. SiO_2 exhibits the highest room temperature conductivity, with a value of 1.29 x10^{-5} S cm^{-1} compared with the conductivity of PLA, 9.46 x 10^{-12} S cm^{-1}. The ionic conductivity of the polymer electrolytes increases with increasing the content of salt and shows the salt is main contributor to ionic conductivity. The increase in conductivity is due to the reduction in crystalline phase upon the addition of salt, plasticizer and filler as evidenced from the XRD analysis. The intensities of the crystalline peaks of the XRD pattern decrease and the area below the peaks broadens. All of this may be related to a possible enhancement in the segmental flexibility of polymeric chains and the disordered structure of the electrolyte where the lithium ion motion taking place in the amorphous phase is facilitated compared to the pure PLA sample. An additional increase of ionic conductivity due to addition of filler SiO_2 which can be explained by the availability of extra hopping sites for migrating ionic species due to the formation of transient H-bonding with O–OH groups at the filler surface. SEM images shows changes in solid polymer electrolytes surface that lead the increasing in conductivity upon addition of salt, plasticizer and filler.

References

1. J. L. Schaefer, Y. Y. Lu, S. S. Moganty, P. Agarwal, N. Jayaprakash, & L. A. Archer, *Springer*, 19. (2011)
2. C. Fonseca, & S. Neves, *J. Power Source*, *159* (2006) 712-716.
3. I. Vroman, L. Tighzert, *Materials* 2 (2009) 307
4. K.V. Pradeep, G. Shikha, *Ionics* 17 (2011) 479.
5. P.V. Wright, Br. Polym. J. 7 (1975) 319
6. M.B. Armand, J.M.D. Chabagno, M. Dulcot, in: P. Vashista, J.M. Mundy, G.K. Sherroy (Eds.), Fast-Ion Transport in Solids, NorthHolland, Amsterdam, 1979.
7. C. Fonseca, D. S. Rosa, F. Gaboardi, & S. Neves, *J. Power Source, 155* (2005) 381-384.
8. D.F. Vieira, C.O. Avellaneda, & A. Pawlicka, *Electrochim. Acta,53 (2007) 1404-1408.*
9. Y.X. Xu, K.M. Kim, M.A. Hanna, & D. Nag, *Industrial Crops and Products, 21 (2005) 185-192.*
10. Y. M. Fu, *Materials Letters , 57* (2003)1759-1764.
11. A. M. M. Ali, N. S. Mohamed, & A. K. Arof, *J. Power Sources , 74* (1998) 135-141.
12. R. Mishra, &, K. J. Rao, *Solid State Ionics , 106* (1998) 113-127.
13. D. Saikia, & A. Kumar, *European Polymer Journal*, 41 (2005) 563–568.
14. H.J. Rhoo, H.T. Kim, J.K. Park, & T.S. Hwang, *Electrochim. Acta , 42* (1997) 1571.
15. S. Ramesh, C.W. Liew , E. Morrisb, & R. Durairajb, *Thermochimica Acta , 511* (2010) 140-146.
16. R. Baskaran, T. Hattori, J. Kawamura, N. Kuwata, & S Selvasekarapandian, *Solid State Ionics, 177* (2006) 2629-2682.
17. S. Rajendran, M. Sivakumar, & R. Subadevi, *Materials Letter, 58* (2004) 641-649.
18. S. Ramesh, & A. Arof, *J. Power Source, 9* (2001) 41-47.
19. M. R. Johan, H.S. Onn, S. Ibrahim, S. M. Yassin, & Y.H. Tan, *Solid State Ionics , 196* (2011) 41-47.