Electrical Properties Study of Solid Polymer Electrolyte based on PolyCaproLactone/LiCF$_3$SO$_3$ Added Plasticizer

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Abstract. The electrical properties of solid polymer electrolyte based on biodegradable polymer PolyCaprolactone (PCL)/LiCF$_3$SO$_3$ with PC plasticizer addition have been studied. Polymer electrolyte membranes were prepared by solution casting technique by varying propylene carbonate (PC) composition (0-60) % weight. The membranes were characterized by the Electrical Impedance Spectroscopy at room temperature to measure its ionic conductivity and other electrical properties such as dielectric constant and tangent loss. The PCL/LiCF$_3$SO$_3$ system containing 20% weight PC plasticizer exhibits the highest conductivity of 4.92 x 10^{-4} S/cm at room temperature. The dielectric constant shows decreases with frequency increasing and it depends on dissociation of ions in the polymer electrolyte system. The tangent loss suggests that there are relaxing dipoles in the polymer electrolyte that shift toward higher frequency region. The membrane microstructure also investigated by XRD and the result showed that the PC plasticizer made the PCL/LiCF$_3$SO$_3$ system become more amorphous

Keywords: PCL/LiCF$_3$SO$_3$, polymer electrolyte, propylene carbonate (PC), electrical properties

1. Introduction
Polymer electrolytes represent an attractive class of solid state materials that exhibit the benefit of various desirable properties such as safety, high flexibility, mechanical stability, multiple charging/discharging cycle and ease fabrication into desired shapes and sizes and their capability to form electrode-electrolyte contact. The solid polymer electrolyte (SPE) is an alternative substitute for the liquid electrolyte in the electrochemical device such as battery. In the battery cell SPE can also separate the two electrodes electronically to prevent short-circuit. Solid polymer electrolytes are essentially polymer salt complexes formed by incorporation salts in a polymer matrix containing heteroatoms such as O, N, S, F etc as Lewis base which serves to coordinate the cations. The solid polymer electrolytes have many advantages to apply in many devices such as in lithium ion batteries, fuel cells, supercapacitors, solar cells, and electrochromic display devices [1,2].

The most polymer electrolyte studied is poly(ethylene oxide) (PEO) with various inorganic salts dissolved in its matrix. PEO has demonstrated its good performance as a solid polymer electrolyte, however the high degree of crystallinity of PEO restricts its use in battery. A few efforts have already made on natural polymers such as chitosan, cellulose acetate, starch [3-5] and synthetic polymers such as poly(vinyl alcohol) (PVA), poly(vinyl chloride) (PVC) [6,7] to obtain the new polymer electrolytes...
for their application in various electrochemical devices. However there are some disadvantages of these films including poor mechanical properties and low conductivity.

Various approaches have been undertaken by many researcher to achieve higher conductivity and improve the mechanical properties of polymer electrolyte, such as (1) formation cross link networks, (2) polymers blending [8], (3) addition of inorganic filler such as SiO₂, TiO₂ and ZrO₂ [9-12], and (4) plastization [7,13]. In plastization, the low molecular weight plasticizer with high dielectric constant such as ethylene carbonate, propylene carbonate etc are added to the polymer electrolyte. Among of them, plastization is the most effective ways to increase the ionic conductivity. The incorporation of plasticizer will increase ionic conductivity by enhancement the amorphous phase of the polymer electrolyte and increase the flexibility and release the mobile charge carriers due to ion dissolution effect. In addition, plasticizer can increase volume within electrolyte system and decreases viscosity by making the ion mobility became easier [14,15].

In this research, PolyCaprolactone (PCL) is used as the base polymer for studies on lithium conducting membrane. PCL is a synthetic biodegradable polymer that widely used in biomedical application because this polymer is nontoxic and has an excellent level biocompatibility. PCL can make the complex compound by coordinating cations in the salt with the carbonyl group and a Lewis base (ester oxygen). PCL also has low glass transition temperature (−60°C) that allows polymer chain to make segmental motion at room temperature, so that the ions could hop from one complexation site to another easily. A few researchers have attempted to make PCL as polymer electrolyte for battery and supercapacitor application by complexing with various salts [16-18]. In this paper we will report the effect of plasticizer addition to the electrical properties of polymer electrolyte PCL incorporated with LiCF₃SO₃.

2. Experimental method

2.1. Materials and methodology
Polymer Polycaprolactone (PCL) with molecular weight 80,000, Lithium Triflat (LiCF₃SO₃) 99.995% salt and propylene carbonate (PC) as plasticizer were purchased from Sigma Aldrich and used without any purification. Tetrahydrofuran (THF) (p.a) as solvent was purchased from Merck.

Polycaprolactone membrane were prepared by dissolving polycaprolactone (PCL) beads in tetrahydrofuran and stirred up for 3 hours. The lithium salt LiCF₃SO₃ was added to the PCL solution (in weight percent) as much as 20% and stirred up for 2 hours. Then PC plasticizer was added to the solution by varying composition (0, 10, 20, 40, 60) % by weight. The mixture was stirred continuously until homogenous and then poured into a petry dish. The membrane is formed by slow evaporation in a vacuum oven for ±72 hours at 50°C. After that membranes were stored in a desiccators for 2 days to remove any remaining solvent [1].

2.2. Characterization
The impedance measurement is done using HIOKI LCR Hi-Tester Model 3532-50 controlled by computer at room temperature. The membrane was placed between the electrodes and impedance values measured with a range of frequencies from 42 Hz to 5 MHz with AC amplitude of 1.0 Volt. In the plot, an imaginary impedance, Zᵢ at vertical axis versus real impedance, Zᵣ at horizontal with same scale, and the bulk resistance (Rᵣ) of polymer electrolyte is obtained by the intercept of semicircle with the x-axis (Zᵢ) [14]. Hence, The ionic conductivity (σ) of polymer electrolyte membrane can be calculated by using equation (1):

$$\sigma_{dc} = \left(\frac{1}{R_b}\right) \times \left(\frac{d}{A}\right)$$  \hspace{1cm} (1)

Where \(R_b\) is bulk resistance, \(d\) is the thickness of membrane and \(A\) is the surface area of contact [19].
The microstructural studies were analyzed at room temperature by Empyrean PANalytical XRD (45 kV, 40 mA) with Cu-Kα radiation (\(\lambda = 1.5418\) Å) and scattering range angle \(2\theta = (5-60)^\circ\) with a step size 0.02 deg/step.

3. Results and Discussion

Figure 1. Impedance plot of complex PCL/LiCF₃SO₃ and PC plasticizer with varying composition at ambient temperature.

Figure 1 only shows the impedance plot for the highest conductivity sample, and Cole-Cole plot of sample with PC 60% could not be seen because the value is out of range of the graph. Figure 1 shows a typical cole-cole plot for complex PCL/LiCF₃SO₃ with various concentration of PC plasticizer. The complex impedance basically consist of (i) a title spiked, (ii) a depressed semicircle or (iii) a combination of depressed semicircle and title spike. From the plot, it can be observed that these polymer electrolyte mostly show a combination of depressed semicircle in high frequency region and an inclined spike at lower frequencies [20].

Figure 2 show ionic conductivity of all samples as a function of PC concentration. The ionic conductivity of membrane PCL/LiCF₃SO₃ (PC 0%) has value 1.4 x 10⁻⁵ S/cm. The PC plasticizer addition to complex PCL/LiCF₃SO₃ as much 10 w.t% and 20 w.t% can increase the ionic conductivity by one order and get maximum value of 4.92 x 10⁻⁴ S/cm by 20 w.t% plasticizer addition. The increase of ionic conductivity can take place because PC plasticizer could lessen the Coulomb force between cation and anion in the lithium salt that is why more salt could dissociate becomes free mobile ions. In addition, the plasticizer addition can create more pathway for ion conduction and also can increase ionic mobility [7,14]. The plasticizer addition made the polymer electrolyte system more amorphous, hence reduces the energy barriers which enhances the mobility of the ion. However, the ionic conductivity decreased further than 40 w.t% PC plasticizer due to the accumulation of plasticizer cluster, which can block the ions transport within the polymer matrix. Shaima et.al. reported that while EC plasticizer was added to CuI/PVA nanocomposite, the ionic conductivity would increase from 1 x 10⁻⁷ to 1 x 10⁻⁵ S/cm [14]
Figure 2. Ionic Conductivity of PCL/LiCF₃SO₃ as a function of PC plasticizer concentration.

The best way to describe the ionic conductivity behaviour of polymer electrolyte is by studying its permittivity (dielectric properties). Dielectric constant ($\varepsilon_r$), charge carrier ($n$) and the dissociation energy ($U$) are associated to the equation:

$$\eta = \eta_0 \exp \left( \frac{-U}{\varepsilon_r kT} \right)$$

(2)

From the equation it can be described that, when the dielectric constant ($\varepsilon_r$) increases, the number of charge carrier increases. In polymer electrolytes, ions are the charge carrier where the dielectric constant represents the stored charge in material. While dielectric loss ($\varepsilon_i$) is a measure of energy losses to move ions and align dipoles when the polarity of dielectric field reverses rapidly. From the impedance measurement, $\varepsilon_r$ ($\varepsilon'$) and $\varepsilon_i$ ($\varepsilon''$) can be calculated using the following equation [21]:

$$\varepsilon' = \frac{Z'}{\omega C_0 (Z'^2 + Z''^2)}$$

(3)

$$\varepsilon'' = \frac{Z''}{\omega C_0 (Z'^2 + Z''^2)}$$

(4)

Where $C_0 = \varepsilon_0 A/t$ where $\varepsilon_0$ is the permittivity of the free space, $A$ is the area of the sample and $t$ is the thickness of the sample and $\omega$ is equal to $2\pi f$ which $f$ in frequency taken from the data in Hz [20].

The frequency dependence of dielectric function of solid materials reflected the dynamic response of the constituents of the solid. Figure 3(a) and (b) show the frequency dependence of the dielectric constant ($\varepsilon'$) and the dielectric loss ($\varepsilon''$) corresponding to PCL/LiCF₃SO₃ polymer electrolyte added PC plasticizer. All sample show similar characteristic in which the $\varepsilon'$ is higher at lower frequency due to orientation of polar groups, ions and space charges polarization at these frequencies. In the low frequency region is observed dispersion with a high value of $\varepsilon'$ and $\varepsilon''$ which is attributed to the dielectric polarization effect. Even so, when the frequency is increased, dipoles are not succeed to make parallel with the applied field and they are oscillating begins to lag behind and the $\varepsilon'$ start decrease [22,23].
Figure 3. Frequency dependence of (a) the dielectric constant ($\varepsilon'$) and (b) the dielectric loss ($\varepsilon''$) corresponding to PCL/LiCF$_3$SO$_3$ polymer electrolyte added PC plasticizer.

More over the dielectric loss ($\varepsilon''$) becomes very large at lower frequencies due to free charge motion within the solid materials. The larger value of dielectric loss at low frequencies is occured as a consequence of the existence of mobile charges within the polymer backbone beside the interfacial polarization at PCL and LiCF$_3$SO$_3$ interfaces. At higher frequencies region, dielectric constant decreases rapidly and becoming frequency independent. This is because the charge carriers and dipoles in the polymer chain find it hard to translate and orient, respectively, according to the direction of the applied field. At higher frequency, the electric field periodic reversal occurs so fast that there is no excess ion diffusion in the direction of the field [24,25].

Propylene carbonate that has high dielectric constant is able to dissociate more lithium salt into cations and anions that cause an increasing in number density of mobile ions. This indicates that the increase in conductivity is due to the increase in the concentration of mobile ions. The polarization is due to the charge accumulation decrease, leading to the decrease in the value of $\varepsilon'$ and $\varepsilon''$. Yusof et al.
also reported that the more plasticizer was added, the more salt dissociate become free ions, therefore increased the stored charge in the solid electrolyte [25].

Figure 4 (a) and (b) depict the variation of real part, M’ and imaginary part, M’’ of electric modulus respectively corresponding to PCL/LiCF$_3$SO$_3$ polymer electrolyte added plasticizer. The equations for real electrical modulus M’ and imaginary modulus M’’ can be expresses as follow:

\[
M' = \frac{\varepsilon'}{(\varepsilon'^2 + \varepsilon''^2)} \tag{5}
\]

\[
M'' = \frac{\varepsilon''}{(\varepsilon'^2 + \varepsilon''^2)} \tag{6}
\]

At low frequency regions, both M’ and M” tend towards zero values. The long tail at lower frequency region is attributed to the large capacitance associated with the electrodes. The curves show that both of M’ and M” increase as the frequencies increase, the dispersions are found at higher frequencies. The presence of the peaks in the modulus at higher frequencies for all polymer complexes implies that the polymer electrolyte membranes are ionic conductor [26].

The observed dispersion is mainly due to conductivity relaxation spreading over range frequencies and indicates the presence of a relaxation time. The absence of peak in M’ diagram is due to the fact that M’ in complex dielectric modulus is equivalent to $\varepsilon'$. In Figure 4(a) is shown that the highest conductivity sample (20 w.t% PC) has shifted to higher frequency and has the lowest M’ value results from the increase in the mobility of the polymer segment and charge carriers with the plasticizer addition. As mentioned before plasticizer addition made polymer electrolyte more amorphous that make the orientation of the charge carriers and molecular dipoles become easier.

The M’’ curves of the ion conducting electrolyte exhibit a relaxation peak in high frequency region corresponding to the ionic conductivity relaxation time. In Figure 4(b) there are no peak of M’’ can be observed that is due to the experimental frequency limitation. So it couldn’t be determined the exact value of ionic conductivity relaxation frequency ($f_\sigma$) and ionic conduction relaxation time ($\tau_\sigma$) [20,26].

Figure 5 depicts the variation in tangent loss as a function of frequency of PCL/LiCF$_3$SO$_3$ membrane for different concentration of PC plasticizer and measured at room temperature. The loss spectra characterized by peak appearing at high frequency region for both plasticizer free PCL/LiCF$_3$SO$_3$
and plasticized PCL/LiCF$_3$SO$_3$ samples. This suggests the existence of dipole dipole relaxation in all the samples. Relaxation occurred as a result of ionic charge carriers within polymer materials obeying the change direction of the applied field. From Figure 5 it is observed that the peak frequency shifted towards higher frequency as the plasticizer concentration increases until 20 w.t%. The peak shift towards higher frequency indicates quicker relaxation time. The peak intensity suggests the easiness of ion movement within polymer matrix. Beyond 40 w.t% plasticizer addition the tangent δ peaks shift towards lower frequency. This due to the excessive plasticizer will accumulate to make cluster that make ion movement become slower. On addition of plasticizer there is increasing in the amorphous phase in the PCL membrane as confirmed by XRD data below. The small and mobile PC molecule can accelerate the segmental motion by increasing the existing free volume. Thus, the relatively fast segmental motion coupled with mobile ions enhances the transport properties on plasticization [15,27].

![Figure 5](image)

**Figure 5.** Frequency dependence of tangent δ corresponding to PCL/LiCF$_3$SO$_3$ polymer electrolyte with different concentration of PC plasticizer.

Figure 6 depict the XRD pattern of PCL/LiCF$_3$SO$_3$ complexes polymer electrolyte with various compositions of PC plasticizer measured at room temperature. There are no difference XRD pattern with the previous research by Yulianti [28]. There are three sharp diffraction peaks in pure PCL and these peaks seem at 2θ = 21.2, 22.1 and 23.79 angles which are plane of (110), (111), and (200) of the orthorhombic crystal system respectively. These sharp peaks are recognized as the crystalline phase of PCL, which comes from the arrangement of polymer side chains caused by the intermolecular interaction between PCL chains through the hydrogen bonding. Besides to these crystalline peaks, there is a small continuous spectrum centered on 2θ = 21.0° that confirms the film is semicrystalline consisting of both crystalline and amorphous phases.
The addition of PC plasticizer to the polymer complexes PCL/LiCF$_3$SO$_3$ have not much changed in the PCL X ray diffraction pattern. The addition of 10 wt.% plasticizer has not changed the PCL diffraction pattern significantly, there are slightly broadening of the three peaks. The addition of 20% plasticizer and more causes the diffraction peaks intensity decreasing and the diffraction peaks became broader. This indicates that there is phase transformation from crystalline into an amorphous phase due to polymer plasticization leads to polymer chains separation followed by the structure rearrangement. The more the amorphous phase is formed the conductivity of the electrolyte polymer will increase. The plasticizer addition can create more free volume in polymer matrix because swelling effect so that Li ions transport become easier. The result inferred from XRD study is in good agreement with conductivity measurements as described previously.

4. Conclusion
Solid polymer Electrolyte based on PolyCaproLactone/LiCF$_3$SO$_3$ complexes with PC plasticizer addition have been success prepared by solution casting method. The electrical properties of membrane polymer electrolyte consist of ionic conductivity, dielectric permittivity, electrical modulus and tangent loss have been studied to investigate the effect of plasticizer addition. The PCL/ LiCF$_3$SO$_3$ complex with 20 w.t% PC plasticizer addition has the highest ionic conductivity value of 4.92 x 10$^{-4}$ S/cm, increase by one order of magnitude from 1.40 x 10$^{-5}$ S/cm for unplasticized membrane. The dielectric permittivity study shows that the PC plasticizer addition proposes that number of charge carriers influences the increase in conductivity significantly.

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