

The Effect of Plasticization on Properties of Polymer Electrolyte PVDF Incorporated with LiPF₆

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Diterima: 10-Feb-2016

Diperbaiki: 18-Mar-2016

Disetujui: 24-Mei-2016

ABSTRACT

The Effect of Plasticization on Properties of Polymer Electrolyte PVDF Incorporated with LiPF₆. The effect of plasticization on properties of polymer electrolyte PVDF incorporated with LiPF₆ has been studied. Ethylene carbonate with high dielectric constant was used as the plasticizer and added with various compositions (0-60% w/w). The polymer electrolyte thin films were prepared by solution casting technique. The successful of doping of the polymer with lithium salt and plasticizer has been confirmed by Fourier transformation infra red spectroscopy (FTIR) by analyzing the C-F vibration region of the polymer. Microstructure and surface morphology were studied by X-ray diffractometer (XRD) and Scanning Electron microscope (SEM), respectively. The thermal properties of polymer electrolytes studied by Differential Scanning calorimeter has shown that the plasticizer addition to PVDF promotes a decreasing in the crystallinity degree. The electrical property studies revealed that the highest conductivity was $3.46 \times 10^{-4} \text{ Scm}^{-1}$ obtained with addition of 60% w/w plasticizer. The study of tangent loss suggests that there are relaxing dipoles in the polymer electrolyte that shift towards higher frequency region.

Keywords: PVDF, LiPF₆, plasticizer, ethylene carbonate

ABSTRAK

Pengaruh Plastisizer terhadap Sifat Polimer Elektrolit PVDF yang telah Ditambah Garam LiPF₆. Telah dipelajari pengaruh plastisizer terhadap sifat polimer elektrolit PVDF yang telah ditambah garam LiPF₆. Etilen karbonat dengan konstanta dielektrik tinggi digunakan sebagai plastisizer dan ditambahkan dengan variasi konsentrasi (0-60% b/b). Lembaran tipis polimer elektrolit dibuat dengan metode casting. Keberhasilan doping polimer dengan garam litium dan plastisizer

dikonfirmasi menggunakan Fourier transformation infra red (FTIR) melalui analisis daerah vibrasi ikatan C-F dari polimer. Struktur mikro dan morfologi permukaan dipelajari menggunakan X-ray diffractometer (XRD) dan Scanning Electron microscope (SEM). Sifat termal polimer elektrolit yang diamati menggunakan Differential Scanning Calorimeter (DSC) memperlihatkan bahwa penambahan plastisizer ke PVDF menurunkan derajat kristalinitas polimer tersebut. Nilai konduktivitas listrik tertinggi diperoleh sebesar $3,46 \times 10^{-4} \text{ Scm}^{-1}$ dengan penambahan plastisizer sebanyak 60% b/b. Perhitungan nilai loss tangent menunjukkan terjadinya relaksasi dipol di polimer elektrolit yang bergeser ke daerah frekuensi yang lebih tinggi.

Kata Kunci: PVDF, LiPF₆, plastisizer, etilen karbonat

INTRODUCTION

Solid polymer electrolyte have attracted increasing interest in the last few decades because of their potential applications as solid electrolyte in electrochemical devices such as fuel cells, super capacitors, sensors etc., in addition its application in batteries [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 been made on natural polymers such as chitosan, cellulose acetate, starch [3-5] and synthetic polymers such as poly(vinyl alcohol) (PVA) and poly(vinyl chloride) (PVC) [6-7] to obtain the new polymer electrolytes for their application in various electrochemical devices. However, there are some major drawbacks of these films including poor mechanical properties and low conductivity.

Various approaches have been undertaken by many researchers 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) plasticization [7,13]. Among them, plasticization is the most effective way to increase the ionic conductivity. In plasticization, the low molecular weight and high dielectric constant plasticizer, such as ethylene carbonate, propylene carbonate, etc. are added to the polymer electrolyte. The incorporation of plastisizer will increase ionic conductivity by enhancement the amorphous phase of the polymer electrolyte, increase the flexibility and release the mobile charge carriers due to ion dissolution effect. In addition, plasticizer can increase volume within electrolyte system and decrease viscosity by making the ion mobility became easier [14,15]. Ethylene carbonate was chosen as plastisizer ini this work, because it has the

highest dielectric constant ($\epsilon = 90.5$, 40°C) among cyclic carbonates plasticizer and widely used as solvent in Li-batteries [16].

In this research, PVDF is used as the base polymer for study on lithium conducting film. PVDF is a polymer that has high dielectric constant ($\epsilon = 8.4$) and widely used in lithium battery. Many researchers have implemented to modify this polymer such as PVDF with LiClO_4 and TiO_2 [17], PVDF with CNT [18], and PVDF with LiCF_3SO_3 [19]. In this paper, we will report the effect of plasticizer addition to the properties of polymer electrolyte PVDF incorporated with LiPF_6 .

EXPERIMENTAL METHODS

Preparation of Polymer Electrolytes

The polyvinylidene fluoride (PVDF) with MW = 534,000 and ethylene carbonate (EC) were purchased from Sigma Aldrich and used without further purification. Lithium hexafluorophosphate (LiPF_6) with Mw = 151.91 g/mol was also obtained from Sigma Aldrich and kept in glove box prior to use as the incorporating salt. Proton conducting polymer electrolytes were prepared by solution casting technique, consisting of PVDF complex with LiPF_6 20 wt. % based on the previous work [20]. PVDF was dissolved in N-methyl-2-pyrrolidone (NMP) at 50°C for 3 h followed by the addition of LiPF_6 . The mixture was stirred continuously with magnetic stirrer until complete dissolution was obtained. Different weight % of EC in the range 20 to 60 wt. % were added into the solution and continued stirred until homogenous solution was obtained. The solutions were then cast into several petri dishes and allowed to slow evaporation at 50°C in vacuum oven until solvent free films were obtained. The dry films were kept in a glass desiccator with silica gel desiccants for further drying.

Characterizations

Shimadzu IRPrestige-21 Fourier transform infrared (FTIR) spectrometer was used to record the FTIR spectra in the transmission mode in the wavenumber range $400\text{-}4000\text{ cm}^{-1}$. Structural studies were performed at room temperature using Empyrean PANalytical XRD with monochromatic $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$) at 40 kV, 30 mA and scattering range angle was from $2\theta = 5 - 60^\circ$ with step size of 0.02° . Thermal analysis was performed with JADE DSC Perkin Elmer system at a heating and cooling rate of $10^\circ\text{C}/\text{min}$ under dry nitrogen atmosphere. Melting temperature T_m and ΔH_m of PVDF were determined from the second heating scan. The surface morphology of polymer electrolytes were studied by the

Scanning Electron Microscope (SEM) type JSM-6510LA from JEOL used a gold coated film samples. The impedance was measured by using HIOKI 3532-50 LCR HiTester that was interfaced to a computer within the 50 to 5 MHz frequency range at room temperature. The PVDF films were cut into a suitable size and coated with silver paste, then sandwiched between the stainless steel blocking electrodes. The ionic conductivity (σ) then was calculated using the equation $\sigma = (1/R_b) (t/A)$ where R_b is the bulk resistance, t is the thickness of the film and A is the electrode-electrolyte contact area. The total ionic transference number was measured by polarization technique. A d.c. voltage source was used at a constant dc potential of 1.5 V to polarize the cell. The polymer film was sandwiched between two blocking electrodes, and connected in series to an ammeter and a switch.

RESULT AND DISCUSSION

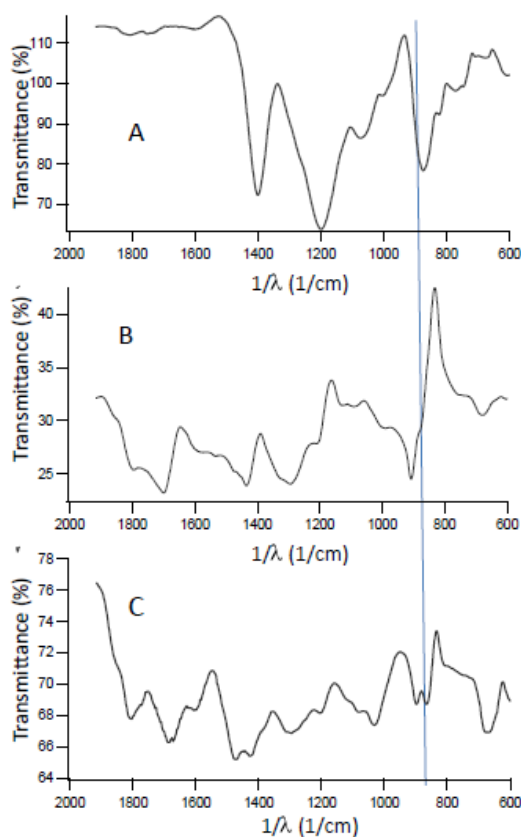


Figure 1. FTIR spectra for (A) PVDF, (B) PVDF + LiPF₆, and (C) PVDF+LiPF₆ + EC

The objective of performing FTIR was to confirm molecular interaction between polymer, lithium salt and plasticizer by monitoring the band shifts of the certain functional group. Figure 1 shows the spectra of selected samples for the system in the region of 600-2000 cm^{-1} . In Figure 1(A), the absorption peak appeared at 1403 cm^{-1} was attributed to CH_2 wagging vibration. The C-C band of PVDF was observed at 1185 cm^{-1} and the C-C-C and C-F band appeared at 878 and 840 cm^{-1} , respectively [21]. The spectrum 1(B) and 1(C) are slightly different with pure PVDF (Figure 1A), in which the peaks intensities become lower. There is peak shifted to higher wavenumber (showed with blue line). The shifted peak is C-F band at $\pm 860 \text{ cm}^{-1}$. Figure 1(B) reveals that there is interaction between fluorine atoms of PVDF with LiPF_6 salt. Figure 1(C) shows the FTIR spectrum PVDF containing LiPF_6 and EC. The peak C-F band has shifted to higher wavenumbers. This can be related with the amorphous characteristic of the material or solvation.

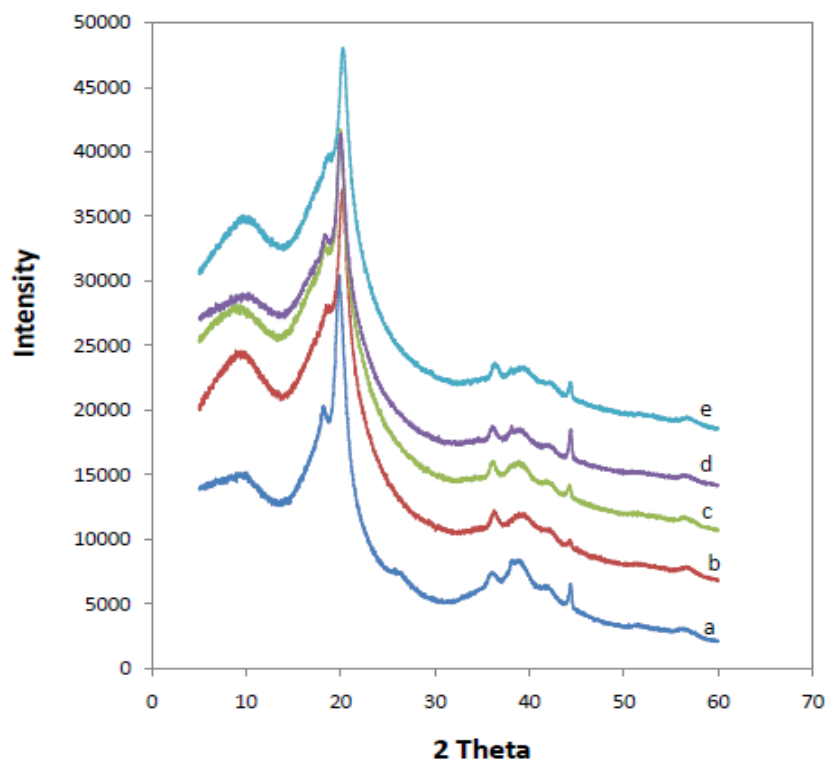


Figure 2. Diffraction pattern of (a) PVDF, (b) PVDF+ LiPF_6 , (c). PVDF+ LiPF_6 +EC 20% (d) PVDF+ LiPF_6 +EC 40% (e).PVDF+ LiPF_6 +EC 60%

Figure 2a-e represent the diffraction pattern for PVDF, PVDF incorporated with LiPF_6 salt, and PVDF/ LiPF_6 with different EC content of

20-60 wt. %, respectively. It was showed in Figure 2(a) that PVDF has sharp diffraction peak at $2\theta = 20.5^\circ$ and broad peak at $2\theta \sim 40^\circ$. This diffraction pattern was similar to that obtained by previous researchers [20]. The addition of LiPF₆ salt did not influence the sharp peak, but the intensity of the broad peak is decreased, suggest a decrease in degree of crystallinity of PVDF (b). The C-F bond in PVDF can form a weak bonding with the lithium ion that can damage crystallinity. The absence of lithium salt diffraction peaks in complex PVDF film reveals that the salt distributed homogeneously. The characteristic peak intensity of PVDF also decreased with increasing EC plasticizer. Polymer plasticization leads to polymer chains separation followed by the structure rearrangement. This in turn results in decrease crystallinity of PVDF that become more amorphous [19,20].

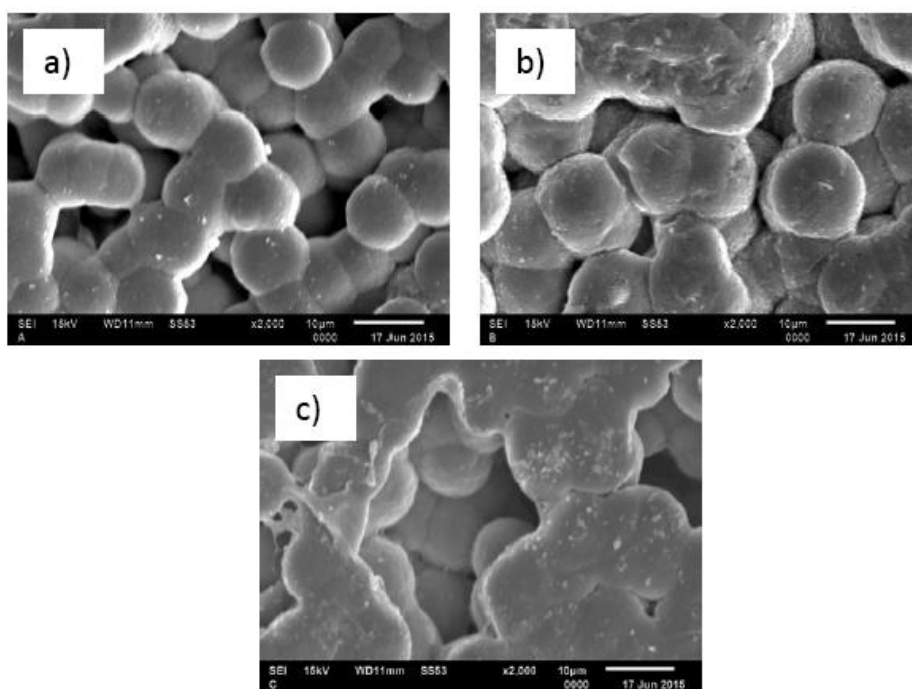


Figure 3. SEM Micrograph (2000x) of (a) PVDF, (b) PVDF+LiPF₆, (c) PVDF+LiPF₆ + EC

To investigate the morphology of the film surfaces and the compatibility between various components, the SEM technique was performed and observations were made with a magnification of 2000x. Figure 3 shows the micrograph of selected samples. It is shown that PVDF film surface (a) forms a spherical grain with a size of about 10 μm and porously. Because PVDF is a polymer having high dielectric constant, its surface tension is also high. With the lithium salt addition, there is interaction

between salt and functional group of polymer and affects the surface tension [20]. The spheres become swelling and larger (Figure 3(b)). The addition EC plasticizer results in the dissolution of the polymer, fills the pores and EC plasticizer molecules can also reduce surface tension. This will facilitate the movement and diffusion of polymer chains at grain boundaries which results spherical grains tend to adhere each other [14].

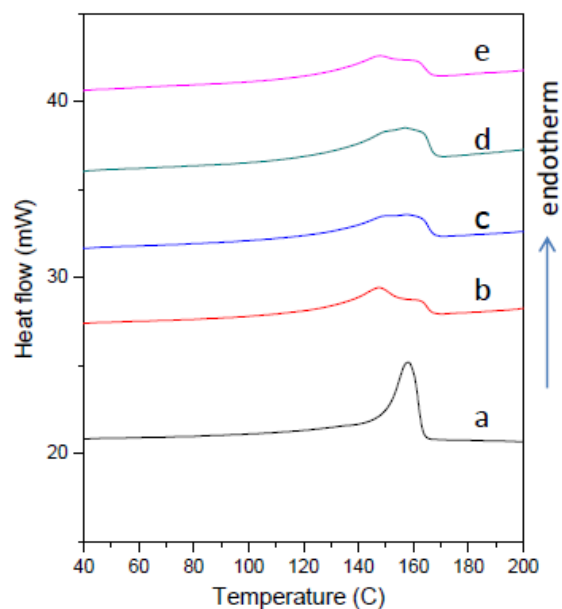


Figure 4. Second scan of DSC curves

Differential scanning thermogram of all PVDF samples is shown in Figure 4. DSC curves show the endothermic melting points for all samples. The PVDF film has sharp peak melting point and its melting point is 159.1°C. The addition of lithium salt made endotherm peak become broader and the melting temperature only slightly decreases. EC plasticizer addition also made endotherm peak become broader. The value of enthalpy (ΔH) of PVDF film become lower with the lithium salt and plasticizer addition, because there are interaction between all components that change PVDF polymer crystal structure become amorphous [22]. The crystallinity (χ) has been calculated by assuming that pure PVDF is 100% with the equation $\chi = \Delta H / \Delta H^\circ$ (where ΔH° is enthalpy PVDF and ΔH is related to salt and plasticizer in the polymer and tabulated in Table 1. It is shown in Table 1 that crystallinity (χ) is suppressed in the presence of lithium salt and plasticizer. This trend agrees with XRD curves aforementioned above.

Table 1. Enthalpy and cristallinity of PVDF film

Sample name	Sample	ΔH (J/g)	χ (%)
a	PVDF	31.57	100
b	PVDF + LiPF ₆	23.99	76
c	PVDF+LiPF ₆ +EC 20%	21.65	68.6
d	PVDF+LiPF ₆ +EC 40%	26.60	84.3
e	PVDF+LiPF ₆ +EC 60%	21.21	67.2

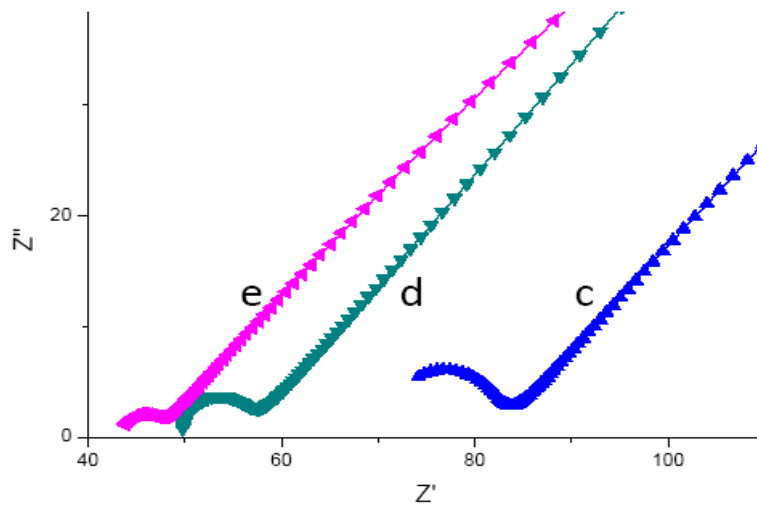


Figure 5. Impedance plot of PVDF+LiPF₆ with different wt.% EC (c) 20, (d) 40, and (e) 60%

The conductivities of all samples were investigated at room temperature over a wide range frequency, 50 Hz - 5 MHz. The complex impedance plot for PVDF +LiPF₆ film with different EC content is shown in Figure 5. Generally, the plot consists of a high frequency depressed semicircle represented by a frequency capacitor (C) parallel to a bulk resistor (R_b) and a low frequency spike represented by a constant phase element (CPE). Extrapolation of the arc to its low frequency intercept on the real Z' axis gives the bulk resistance (R_b) of the samples [23]. By using EIS spectrum analyzer program the R_b value can be determined. The ionic conductivity (σ) of all PVDF film can be calculated using equation:

$$\sigma = \frac{l}{R_b.A} \quad (1)$$

where *l*, *A* and *R_b* are the thickness and cross sectional area and bulk resistance of PVDF film.

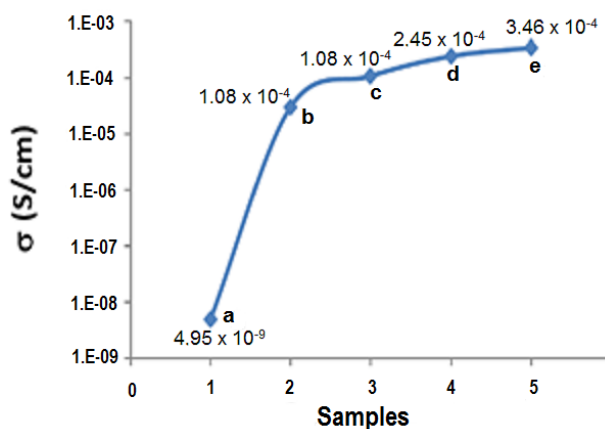


Figure 6. Conductivity of PVDF films

Table 2 and Figure 6 show conductivity of all samples as a function of EC concentration. The conductivity of PVDF film increased by lithium salt addition (sample b) and PVDF+LiPF₆ film (sample c-e) also increased one order of magnitude by plasticizer ethylene carbonate addition. The increase in conductivity occurs because EC can weaken the Coulomb force between cation and anion of the lithium salt that is why more salt dissociates becomes free mobile ions [14,24]. Moreover, the plasticizer addition can create more pathways for ion conduction and can also increase ionic mobility. The highest conductivity obtained is $3.46 \times 10^{-4} \text{ Scm}^{-1}$ with the 60% w/w plasticizer addition. Shaima et al. [14] reported that when ethylene carbonate was added to CuI/PVA nanocomposites, the conductivity increased from 1×10^{-7} to $1 \times 10^{-5} \text{ Scm}^{-1}$.

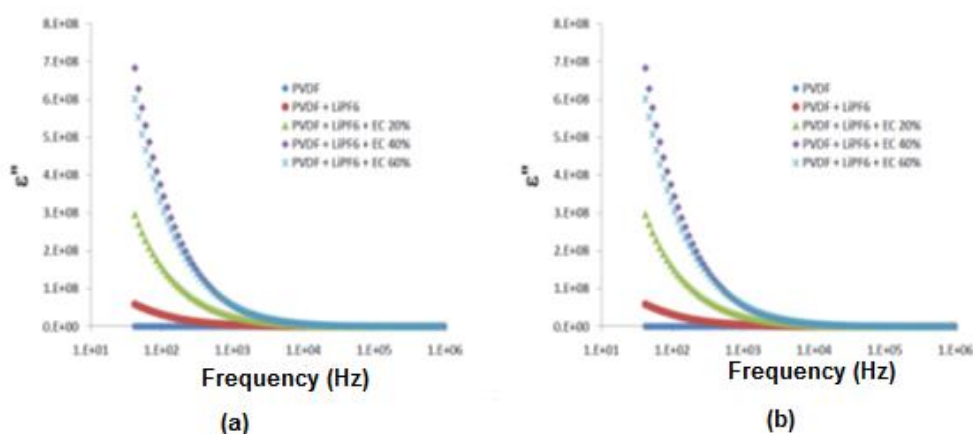


Figure 7. Variation of (a) dielectric constant ϵ' and (b) dielectric loss ϵ'' with frequency at room temperature

To understand the polarization effect at the electrode/electrolyte interfacial, it can be done by studying on the permittivity in polymer electrolyte films. Dielectric constant (ϵ') is a representative of stored charge in a material while dielectric loss (ϵ'') is a measure of energy losses to move ions and align dipoles when the polarity of dielectric field reverses rapidly. From the impedance measurement, ϵ' and ϵ'' can be calculated using the following equations.

$$\epsilon' = \frac{Z'}{\omega C_o (Z'^2 + Z''^2)} \quad (2)$$

$$\epsilon'' = \frac{Z''}{\omega C_o (Z'^2 + Z''^2)} \quad (3)$$

The frequency dependence of dielectric function of solid materials reflects the dynamic response of the constituents of the solid. Figure 7(a) and (b) show EC concentration of dielectric constant and dielectric loss, respectively. Figure 7 also depicts that the dielectric constant decreases with increase the frequency. In the low frequency region is observed dispersion with a high value of ϵ' and ϵ'' which is attributed to the dielectric polarization effect. Moreover, the dielectric loss (ϵ'') becomes very large at lower frequencies due to free charge motion within the solid materials. The larger value of dielectric loss at low frequencies could be due to the existence of mobile charges within the polymer backbone beside the interfacial polarization at PVDF and LiPF₆ interfaces. At higher frequencies region, dielectric constant decreases rapidly and is 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 high frequency, the electric field periodic reversal occurs so fast that there is no excess ion diffusion in the direction of the field [25-26].

EC that has high dielectric constant is able to dissociate more lithium salt to cations and anions resulting in an increase 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 ϵ' and ϵ'' . 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 [26].

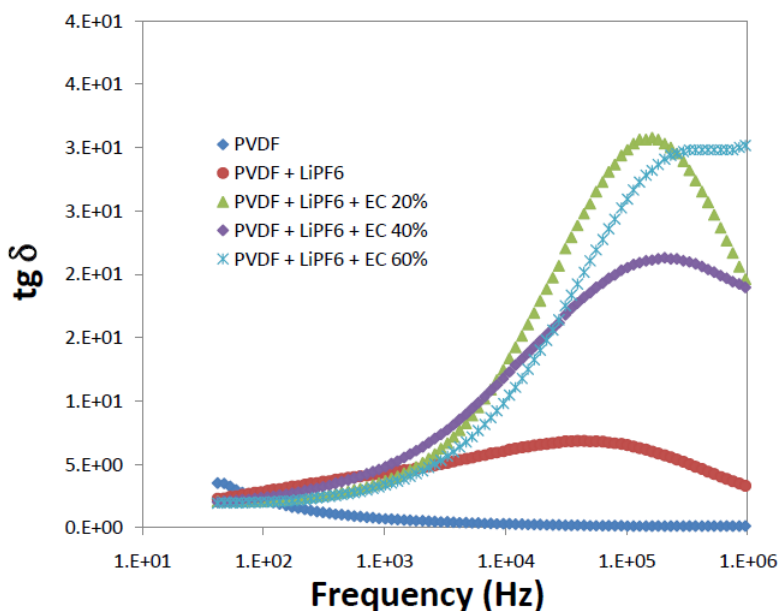


Figure 8. Variation of tangent δ PVDF thin film with frequency for different concentration of EC

The variation in tangent loss as a function of frequency of PVDF films for different concentration of EC and measured at room temperature is presented in Figure 8. The loss spectra characterized by peak appearing at high frequency region for both plasticizers free (PVDF + LiPF₆) and plasticized PVDF 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 8, it is observed that the peak frequency shifted towards higher frequency as the plasticizer concentration increases. The peak shift towards higher frequency indicates quicker relaxation time. The peak intensity suggests the easiness of ion movement within polymer matrix. On addition of plasticizer there is an increase in the amorphous content in the PVDF film as confirmed by XRD and DSC data. The small and mobile EC 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 [15,19].

CONCLUSION

The study of 20 wt.% LiPF₆/PVDF polymer electrolyte with different concentration of EC shows significant effect of structure, thermal stability,

ionic conductivity, permittivity and tangent delta. Both T_m and ΔH show decrease with increasing EC concentration, indicates the polymer structure become more amorphous. The ionic conductivity of 20% wt.% LiPF₆/PVDF increased by one order of magnitude from 3.02×10^{-5} S/cm (without EC plasticizer) to 3.46×10^{-4} S/cm with the 60% w/w plasticizer addition. In permittivity study, ϵ' value increases 10 times showing that EC contributes to higher dissociation rate of charge ions.

ACKNOWLEDGMENT

This project was financially supported by the Center for Science and Technology of Advanced Materials, National Nuclear Energy Agency (BATAN) Indonesia, DIPA 2015 Grant No. 4446.007.001.

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