

Ionic Conduction of Blend Poly (Vinylidene Fluoride-Hexafluoro Propylene) and Poly (Methyl Methacrylate)-Grafted Natural Rubber Based Solid Polymer Electrolyte

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The complex of Poly (vinylidene fluoride-hexafluoro propylene) (PVDF-HFP), Poly (methyl methacrylate)-grafted natural rubber (MG49) (70/30) with lithium trifluoromethane sulfonate (LiCF₃SO₃) based solid polymer electrolyte has been prepared using solution casting technique. The electrochemical impedance spectroscopy (EIS) has been used to measure the ionic conductivity. This work has demonstrated that the addition of an optimum content of LiCF₃SO₃ enhance the ionic conductivity of polymer electrolyte films and conductivity values were found to depend upon the concentration of LiCF₃SO₃. The highest ionic conductivity achieved at $1.97 \times 10^{-4} \text{ S cm}^{-1}$ for 25 wt. % of LiCF₃SO₃ at room temperature. By applying the temperature range from 303 K to 373 K the conductivity rise and the maximum conductivity obtained at $5.65 \times 10^{-3} \text{ S cm}^{-1}$ at 373 K. The interaction between Li ion and F atom in the structure of PVDF-HFP and O atom in MG49 resulting the formation of complex proved by the study of fourier transform infrared spectroscopy (FTIR). The amorphicity and crystallinity of electrolyte films have been characterized by x-ray diffraction (XRD) which indicates decrease in the degree of crystallinity by increasing of salt concentration. Scanning electron microscopy (SEM) appeals that there is no phase separation in the blend. Furthermore the nature of lithium salt has been found to influence the morphology of the polymer-blended electrolytes by improvement of surface morphology from rough to smooth with increasing salt content.

Keywords: PVDF-HFP, MG49, Blend, Solid polymer electrolyte, Ionic conductivity.

1. INTRODUCTION

Demands for solid polymer electrolyte application require a set of properties. Blending is a well-established way to obtain a certain amount of physical properties. As an example, blending

comprising of two or more polymer in which one polymer is adopted to absorb the electrolytes' active species while another provides toughness to the polymer electrolyte films [1, 2].

MG49 is a semi crystalline polymer consists of rubber base and MMA part which lead to formation of a thin, flat and flexible film [3]. Furthermore due to present of carbonyl and ether group in the structure of MG49 formation of complex occur between oxygen atoms and Li^+ ion from salt which is known as coordination bond [4, 5]. PVDF-HFP with unique characteristics such as chemical stability, plasticity, high dielectric constant ($\epsilon = 8.4$), and low glass transition temperature (T_g) applied as an excellent polymer host [6]. Moreover the amorphicity of PVDF-HFP is greater compared to PVDF which is related to the steric hindrance provided by CF_3 pendant group in HFP monomers which is randomly mixed with the VDF monomers in the polymer chain [7]. The amorphous phase of PVDF-HFP has the ability to trap large amount of electrolyte while the crystalline phase acts as a mechanical support for the formation of a free standing film [8].

In spite of above properties, by combination of mentioned properties upon blend of PVDF-HFP and MG49 (70/30) and incorporation of LiCF_3SO_3 as salt the ionic conductivity and mechanical properties of solid polymer electrolyte will improve.

2. EXPERIMENTAL DETAILS

Poly (methyl methacrylate)-grafted natural rubber (MG49) was supplied by Green HPSC Malaysia Sdn. Bhd. Poly (vinylidene fluoride-hexafluoro propylene) (PVDF-HFP) and lithium trifluoromethane sulfonate (LiCF_3SO_3) purchased from Aldrich and Fluka respectively. These materials were used as received without any purification. Solution casting technique has been used to prepare the polymer blend electrolytes. MG49 (30 wt. %) dissolved in tetrahydrofuran (THF: Baker) and maintained for 24 hours. The solution was then stirred for the next 24 hours. PVDF-HFP (70 wt. %) was dissolved in acetone (System) and stirred for 24 hours. Then MG49 solution was added to PVDF-HFP solution and stirred until the solution gets homogenous followed by continuous stirring for 24 hours. Different concentration of LiCF_3SO_3 salt was prepared in glove box separately in THF and stirred for 1 hour then was added to the blend solution and stirred for another 24 hours. Eventually the film of solid polymer electrolyte was obtain by casting the solution on the glass petri dish, and allowed to remove the solvent slowly under fume hood and then further dried under vacuum at 40°C for 24 hours. To prevent contact with air and moisture, prepared film were stored in a desiccator.

Ionic conductivity was conducted at room temperature and at temperature range of 303 K to 373 K by sandwiching the cast films between two stainless-steel electrodes of 16 mm diameter using high frequency resonance analyzer (HFRA) model 1255 with applied frequency from 1 MHz to 0.1 Hz at 100 mV amplitude. The cast films were also subjected to fourier transform infrared analysis (ATR-FTIR) with a Perkin Elmer spotlight 400 imaging system in the frequency range of 650 to 4000 cm^{-1} with the scan resolution of 2 cm^{-1} . X-ray diffraction (XRD) model D-5000 Siemen was used to study the crystalline and amorphous structural behavior of the electrolyte. The data was taken at the diffraction angle 2θ from 10° to 80° at the rate of 0.025°s^{-1} . The morphological and surface properties of polymer electrolyte was studied by scanning electron microscopy (SEM) Philip XL 30 model with

magnifications of 3000×.

3. RESULT AND DISCUSSION

3.1 Ionic Conductivity

The impedance plots of polymer electrolytes are shown in Figure 1 (a) and (b), where the response of impedance consists of a high frequency semicircle and a low frequency spike.

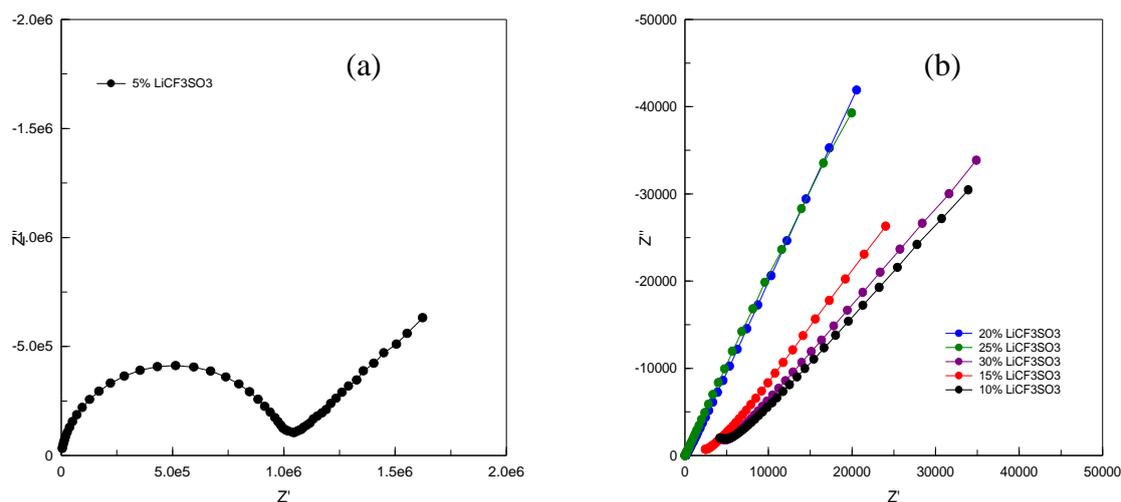


Figure 1. Impedance plot of PVDF-HFP/MG49 (70/30) with a) 5 wt. % LiCF_3SO_3 b) 10 to 25 wt. % LiCF_3SO_3 salt

The observation of high frequency semicircle for 5 wt. % of LiCF_3SO_3 salt (Fig 1 (a)) can be related to parallel combination of resistor and capacitor where the resistor is corresponded to the migration of the ions which take place through the free volume of polymer matrix and the capacitor is referring to the immobile polymer chains [9,10] In other words, a rapid decrease in resistance happened due to ion diffusion inside the electrodes. This can assist to provide a sufficient ion conducting phase inside the electrodes in order to give a high capacitance and low ion-diffusion resistance, thus higher in conductivity[9] In conclusion the high frequency semicircle is due to ion conduction[11] At higher salt concentration above 5wt. % of LiCF_3SO_3 (Fig.1 (b)) the semicircle has been found to be absent. The spike at low frequency is representing the blocking electrode. This suggests that only the resistive component of the polymer prevails [12]. The bulk resistance for all samples has been calculated from the low frequency intercept of the semicircle or high frequency intercept of the spike on the real axis [9]. Result shows that by increasing the salt concentration the bulk resistance R_b decreases which is due to increase in charge carriers. The conductivity (σ) value has been calculated by using following equation $\sigma = [t / (AR_b)]$. Where A is the known area of the electrolyte film, R_b is the bulk resistance and t is the film thickness.

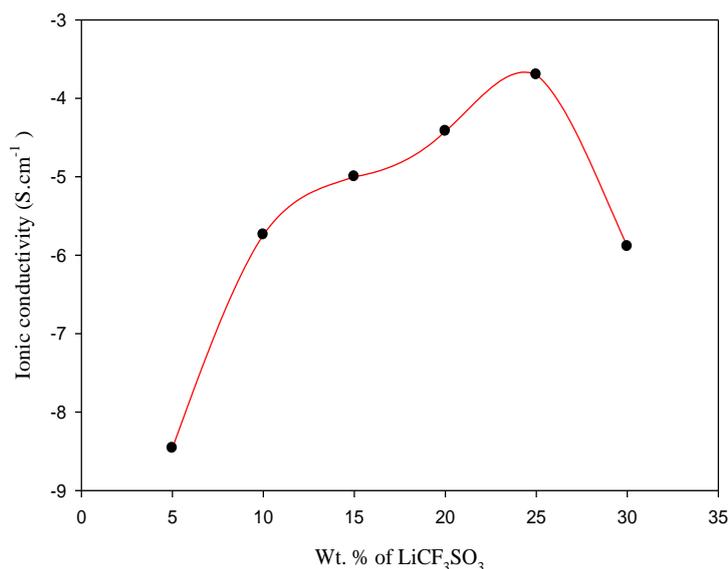


Figure 2. Effect of LiCF₃SO₃ concentration on ionic conductivity

Fig. 2 illustrates that upon addition of salt, ionic conductivity increase gradually from 5 wt % up to 25 wt % of salt. Generally ionic conductivity of a polymer electrolyte depends on the concentration of charge carriers as well as their mobility and cationic and anionic types of charge carriers. The initial increase in conductivity is due to an increase in the number of charge carriers in the matrix and the maximum conductivity is $1.97 \times 10^{-4} \text{ S cm}^{-1}$ at 25 wt. % of LiCF₃SO₃ at room temperature. This value is found to be higher compared to those of PVDF-HFP/MG49/ LiClO₄ [13]. It can be propose that the introduction of LiCF₃SO₃ make the blend of PVDF-HFP/MG49 more elastic, less brittle and finally helped the migration of ion due to specific properties of LiCF₃SO₃ such as low lattice energy, excellent safety as well as stability properties [14]. Future addition of salt (30 wt% of LiCF₃SO₃) caused a drop at conductivity which is mainly due to ion – ion interaction leads to aggregation of ions species so that ion clusters will form hence the number of charge carrier decrease [15]. Fig.3 presents the temperature dependence of the ionic conductivity containing of 25 wt % of LiCF₃SO₃ by Arrhenius model. The temperatures used covered the range of 303 K to 373 K. the conductivity enhanced as the temperature is raised and it reach to $5.65 \times 10^{-3} \text{ S cm}^{-1}$ at 373 K. No linear dependence could be obtained from Arrhenius plots which indicate that the electrolyte is not following Arrhenius rule. Increase in conductivity by increasing of temperature is attributed to segmental motion of polymer electrolyte which let to creation of free volume. The mobility of ions and polymer chain is affected by free volume. The segmental movement allows the ions to hop from one side to another or make a pathway for movement of ions. In other words, translational ionic motion has been facilitated by segmental motion which reflects in ionic motion [16].

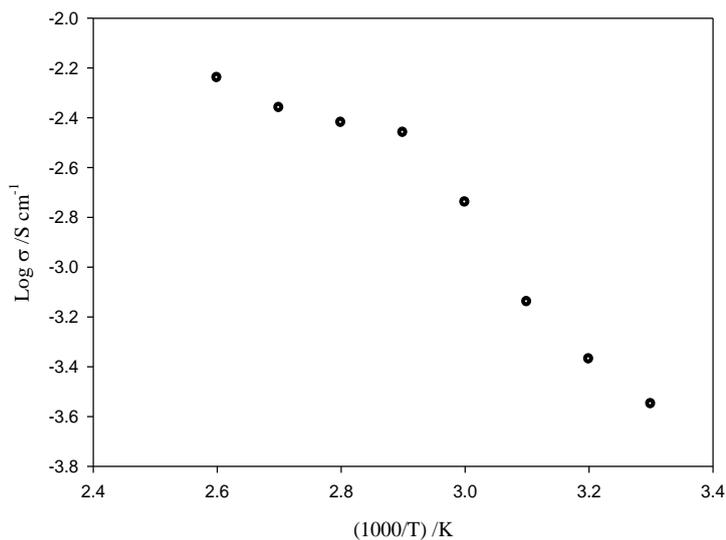


Figure 3. Arrhenius plot of (70:30) PVDF-HFP/MG49 electrolyte at 25 wt. % LiCF_3SO_3 .

3.2. XRD

As it can be seen from Fig. 4, the peaks at $2\theta = 18^\circ$, 20° and 26° represent the semi crystalline of PVDF-HFP polymer [17, 18].

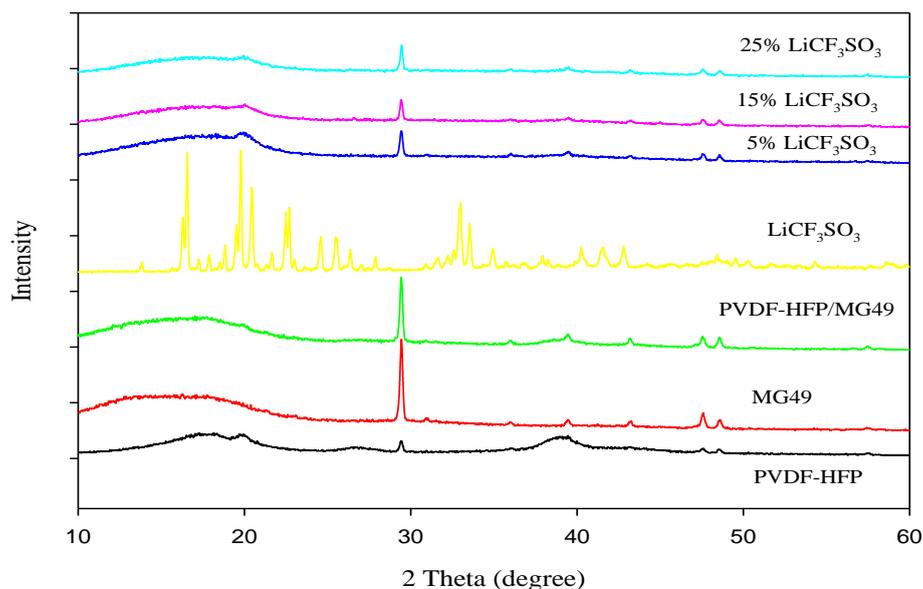


Figure 4. XRD spectra of PVDF-HFP, MG49, PVDF-HFP/MG49 blend, LiCF_3SO_3 and various percentage of LiCF_3SO_3 .

The semi crystalline nature of MG49 was revealed from the hump in the region between 10° to 23° and the intense peak at angles $2\theta = 29^\circ$ correspond to MMA monomer [3, 4]. Upon blending the

crystallinity degree of polymer reduced beside that the hump gets broadened. There is a dramatic change in the structure of polymer electrolyte after addition of LiCF_3SO_3 salt. It is clearly observed that the crystallinity degree of polymer as well as the intensity of MMA monomer peak decreased by increasing of salt concentration which is supported by SEM result. It is noted, the important factor to gain higher conductivity in polymer electrolyte is decrease the crystallinity of polymer where lithium cation can move freely and quickly with the motion of the polymer segments. These results were supported by the electrical impedance spectroscopy (EIS). The LiCF_3SO_3 peaks are not seen in any of the polymer-salt complexes which indicates that the LiCF_3SO_3 solvates very well in the PVDF-HFP/MG49 matrix. The present results support the formation of complex between two polymers and salt and it is in agreement with FTIR results.

3.3 FTIR

It is apparent from spectrum in Fig.5 that α and β crystalline phase (974 cm^{-1} and 838 cm^{-1}) belong to PVDF-HFP are disappeared in the blend while the amorphous phase of PVDF-HFP (871 cm^{-1}) is shifted to higher frequency at 875 cm^{-1} in the blend [6-18]. Therefore it can be concluded that crystallinity of polymer decreased significantly by introducing of MG49 into PVDF-HFP matrix. Moreover the crystalline phase does not appear at the present of LiCF_3SO_3 salt whereas the amorphous part get shifted to higher wave-number at 879 cm^{-1} and the peak become broader. This result is supported by XRD study.

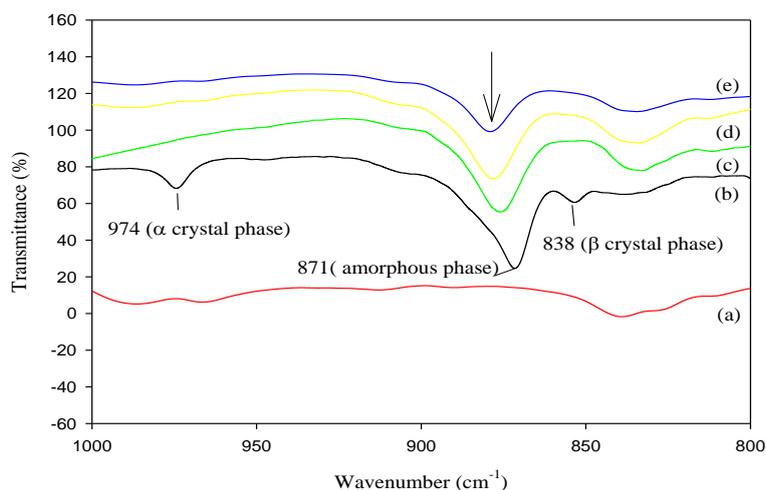


Figure 5. FTIR spectra of (a) Pure MG49, (b) pure PVDF-HFP, (c) PVDF-HFP/MG49 blend, (d) 5 wt % of LiCF_3SO_3 salt and (e) 25 wt % of LiCF_3SO_3 salt in $800\text{-}1000\text{ cm}^{-1}$ wavenumber.

As it shows in Fig. 6 the identified peak at 1063 cm^{-1} assigned to symmetrical stretching mode of CF_2 get shifted to 1069 cm^{-1} through blending. Another important point that was observed in the blend of PVDF-HFP and MG49 is disappearing of some main peaks. As it can be seen from Fig. 6, the bands at 1148 , 1203 , 1179 and 1146 cm^{-1} are assigned to the symmetrical stretching mode of CF_2 , asymmetrical stretching vibrations of the CF_2 group, symmetrical stretching mode of CF_2 and C-O-C asymmetric, respectively in PVDF-HFP and However, it seems that these peaks were not present in the blend [19, 20].

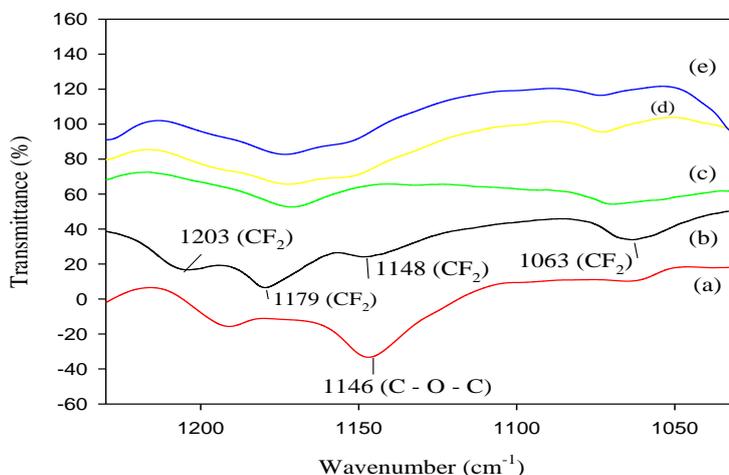


Figure 6. FTIR spectra of (a) Pure MG49, (b) pure PVDF-HFP, (c) PVDF-HFP/MG49 blend, (d) 5 wt.% of LiCF_3SO_3 salt and (e) 25 wt.% of LiCF_3SO_3 salt in $1000\text{--}1250\text{ cm}^{-1}$ wavenumber.

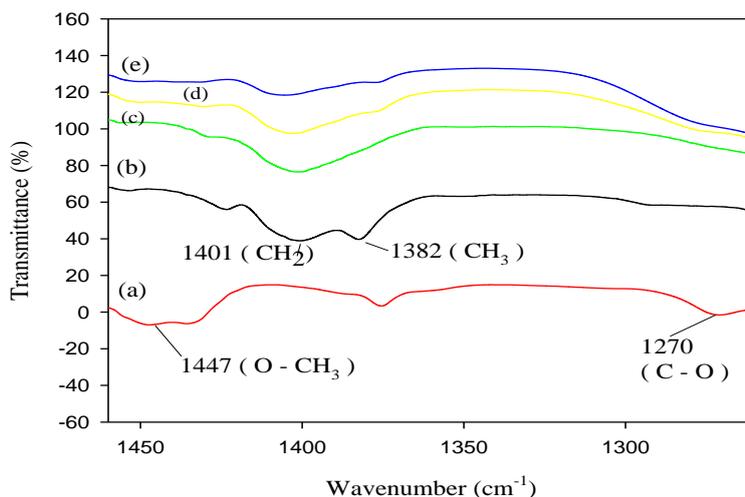


Figure 7. FTIR spectra of (a) Pure MG49, (b) pure PVDF-HFP, (c) PVDF-HFP/MG49 blend, (d) 5 wt.% of LiCF_3SO_3 salt and (e) 25 wt.% of LiCF_3SO_3 salt in $1250\text{--}1500\text{ cm}^{-1}$ wavenumber.

Furthermore the band of C-O symmetric and O- CH_3 in the structure of MG49 and CH_2 wagging which were observed at 1270 , 1447 and 1382 cm^{-1} respectively in Fig. 7 are not detected in

the blend [21-22] The peak corresponding to symmetrical stretching of the carbonyl group ($C = O$) at 1726 cm^{-1} is absent in the blend of PVDF-HFP/MG49 (Fig. 8)) Thus the absent either a shifting in the absorption frequency is a strong evidence to prove the compatibility of PVDF-HFP and MG49 blend. The band ascribed to deformed vibration of CH_2 groups (Fig.7(b)) which is at 1401 cm^{-1} , shifting to high frequency position (1404 cm^{-1}). This is due to the weak interaction between H atoms of CH_2 groups and F atoms of CF_2 groups [19].

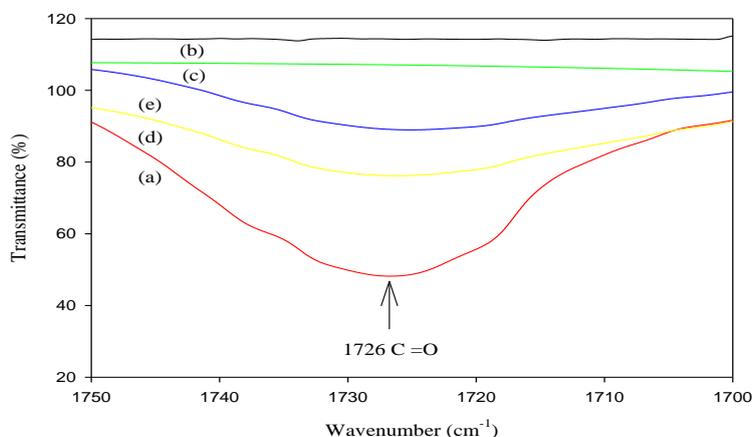


Figure 8. FTIR spectra of (a) Pure MG49, (b) pure PVDF-HFP, (c) PVDF-HFP/MG49 blend, (d) 5 wt.% of $LiCF_3SO_3$ salt and (e) 25 wt.% of $LiCF_3SO_3$ salt in $1700\text{-}1750\text{ cm}^{-1}$ wavenumber.

The FTIR spectrum shows that by addition of $LiCF_3SO_3$ salt into blend some changes have occurred, specially the appearance of some absent peaks. As the percentage of salt is increased the band of polymer shifted slightly with decrease in intensity. The peaks at 1179 , 1382 , 1401 , 1447 and 1726 cm^{-1} shifted to 1173 , 1375 , 1405 and 1725 cm^{-1} at the present of high salt concentration. Upon addition of $LiCF_3SO_3$, was considered to be evidence of specific interaction between Li ions and functional groups ($C-F$) in PVDF-HFP and oxygen atoms in carbonyl group ($C = O$) and ether group ($C-O-C$) of MG49. This seems proof enough for the formation of complex in polymer electrolyte.

3.4 SEM

Figure 9 shows the SEM micrographs of PVDF-HFP/MG49 blend, and PVDF-HFP/MG49 blend with various wt. % of $LiCF_3SO_3$.

The micrograph of PVDF-HFP/MG49 blend (70/30) shows the homogeneous mixture and there is no trace of phase separation (Fig.9 (a)). The existence of micro porous through blending is because of the ability of blended polymer to retention of solvent [18]. Furthermore it is due to solvent evaporations [23] It is clearly observed that the addition of a small amount of salt influence on the structure of blend electrolyte and essentially it reduced the size and number of pores and further

addition of salt causes the well-defined morphology (Fig.9 (b - d)). As it can be seen at high percentage of salt the surface gets smoother. In contrast with less amount of salt (5 wt %), the higher concentration of salt (25 wt %) facilitate more ion transfer hence provide higher ionic conductivity (Fig.9 (d)). These results allow the conclusion that homogeneous polymer electrolytes are formed over all the blend compositions and the complex is quiet compatible.

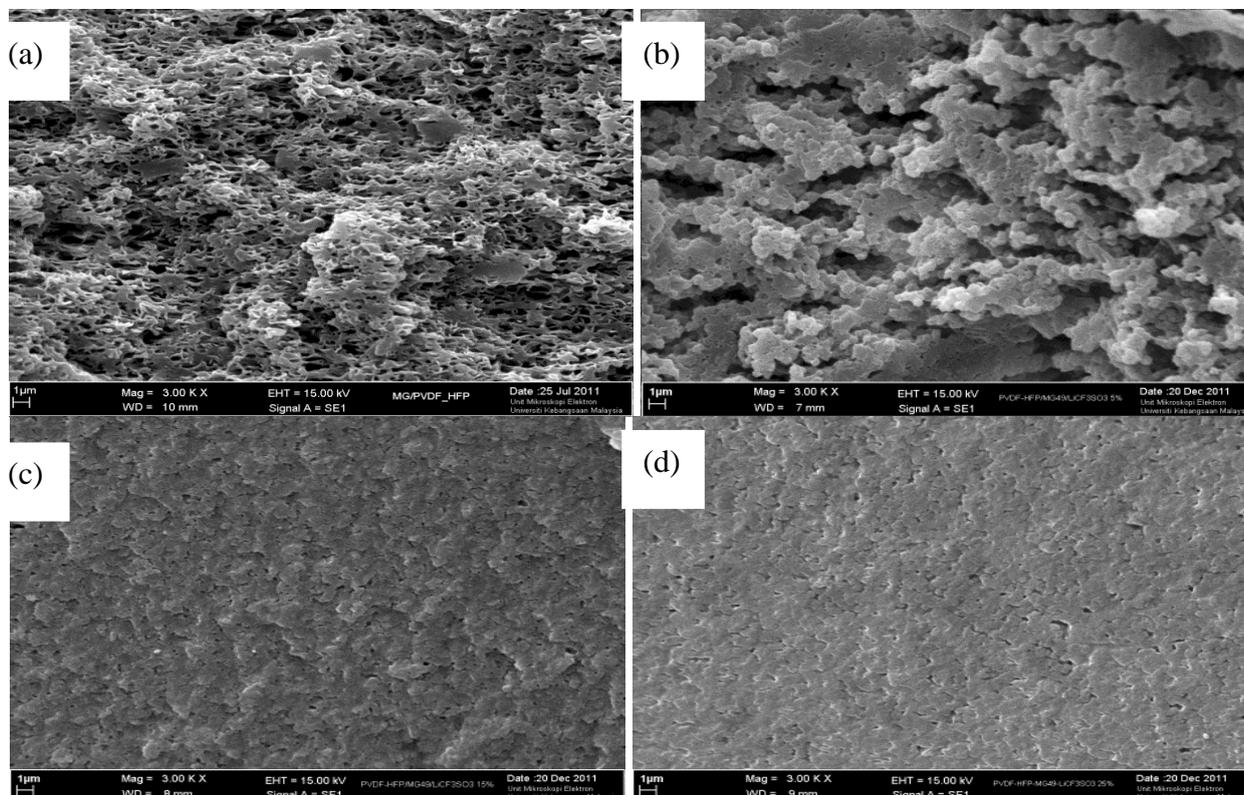


Figure. 9. SEM micrographs (3000 \times) of (a) PVDF-HFP/MG49 blend (b) 5 wt.% LiCF_3SO_3 (c) 15 wt.% LiCF_3SO_3 (d) 25 wt.% LiCF_3SO_3 .

4. CONCLUSIONS

Free standing and flexible polymer electrolyte films based on PVDF-HFP/MG49/ LiCF_3SO_3 have been prepared successfully. The EIS study reveals that conductivity of the electrolytes increases in the order of 10^{-9} to $10^{-4} \text{ S cm}^{-1}$ as the concentration of LiCF_3SO_3 salt increases from 5 to 25 wt.%. FTIR result prove that Li ions interact with functional groups (C-F) in PVDF-HFP and oxygen atoms in carbonyl group (C=O) and ether group (C-O-C) of MG49 and complexation take place in electrolyte furthermore crystallinity of complex reduces which is in agreement with XRD result. The microscopy image confirms the compatibility of complex.

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