

Preparation and Characterization of PVDF-HFP/MG49 Based Polymer Blend Electrolyte

N. Ataollahi¹, A. Ahmad^{1,2*}, H. Hamzah^{1,2}, M.Y.A. Rahman^{3,*}, N.S. Mohamed⁴

¹ School of Chemical Sciences and Food Technology, Faculty of Science and Technology

² Polymer Research Center, Faculty of Science and Technology

Universiti Kebangsaan Malaysia, 43600, Bangi, Selangor, Malaysia

³ College of Engineering, Universiti Tenaga Nasional, 43009, Kajang, Selangor, Malaysia

⁴ Center of Foundation Studies, University Malaya, 50603, Kuala Lumpur, Malaysia

*E-mail: azizan@ukm.my, yusri@uniten.edu.my

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Solid polymer electrolytes comprising poly (vinylidene fluoride-hexafluoro propylene) (PVDF-HFP), Poly (methyl methacrylate)-grafted natural rubber (MG49) and lithium salt (LiBF₄) were prepared by solution casting technique. The membranes were characterized by impedance spectroscopy (EIS), fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD) and scanning electron microscopy (SEM). The electrolyte exhibited the highest room temperature conductivity 2.8×10^{-4} S cm⁻¹ at 30 wt. % of LiBF₄. The conductivity increases with temperature but it does not obey Arrhenius rule. The interaction between lithium ions and polymer host was confirmed by fourier transform infrared spectroscopy. The XRD result confirmed that adding salt led to decrease the degree of crystallinity. The SEM studies showed that the morphology improved in the presence of the salt.

Keywords: Polymer electrolyte, Polymer blend, Ionic conductivity, Arrhenius rule

1. INTRODUCTION

Solid polymer electrolytes have been interesting subject for Li ion batteries due to the various properties such as no leakage behavior, prevention of lithium dendrite growth, flexible geometric shape, higher safety and ease of manufacture [1]. Particular attempts today are focused on improving the ionic conductivity, thermal and chemical stability as well as mechanical strength of polymer electrolyte. Among the variety of methods which have been used to change and improve the properties of polymer electrolyte, blending seems to be a good strategy to hold back the crystallinity and enhance the ionic conductivity [2]. Polymer blend electrolyte comprises at least two polymers which one of the

polymers was applied to absorb the electrolyte's active species while the other one which is tougher and inert, improving the mechanical property of the polymer blend [3]. The main advantages of blend systems are simplicity of preparation and ease of control of physical properties by compositional change [4]. Furthermore, free standing films can be prepared by blending two polymers [2].

Many researches were carried out on Poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) [1,5,6] due to various interesting properties such as high dielectric constant ($\epsilon=8.4$) which support for dissociation of salt, low crystallinity which can improve the ionic conductivity and low glass transition temperature (T_g) of (PVdF-HFP) considered as a suitable polymer host [5,6,7]. PVDF-HFP has excellent chemical stability due to the crystalline vinylidene (Vdf) phase and plasticity, mainly supported by amorphous hexafluoro-propylene (HFP) part [6,8]. The strong electron-withdrawing functional group ($-C-F$) in PVDF-HFP makes this polymer highly anodically stable [9]. Grafted-copolymer of natural rubber with poly (methyl methacrylate) (PMMA), named MG49 has gain attention as polymer host. The oxygen atoms in the structure of MG can act as electron donor atoms. The coordinate bond between Li ions of salt and the oxygen atoms with the lone pair of electron, hence form a polymer complex [10, 11]. Elastic property, soft elastomer nature at ambient temperature and low glass transition temperature, T_g , of modified natural rubber (NR) can assist to improve the contact between an electrolytic layer and an electrode in batteries system apart from convenient elasticity can result in flat thin and flexible film [10,12].

The present work aims to prepare and characterize PVDF-HFP/MG49 based polymer blend electrolyte with various characterization techniques, such as AC impedance spectroscopy, fourier transforms infrared, x-ray diffraction and scanning electron microscopy.

2. EXPERIMENTAL

2.1. Materials

MG49 was commercially obtained from Green HPSC Malaysia Sdn. Bhd. PVDF-HFP and lithium tetrafluoroborate salt ($LiBF_4$) were supplied by Aldrich. All the materials were used without further purification. Solution casting technique was used to prepare the polymer blend electrolytes. MG49 (30 wt. %) was cut into smaller size and dissolved in tetrahydrofuran (THF) for 24 hours. The solution was then stirred by magnetic stirrer for the next 24 hours. PVDF-HFP (70 wt. %) was dissolved in acetone and stirred for 24 hours using magnetic stirrer. These two solutions (PVDF-HFP and MG49) were mixed and stirred to obtain a homogenous solution for another 24 hours. $LiBF_4$ salt solution was prepared separately in tetrahydrofuran and stirred for 1 hour. $LiBF_4$ was added to the blend solution and further stirred for 24 hours. Finally, the blend in solid state was obtained by casting the solution on the glass petri dish, and the solvent was allowed to slowly evaporate in a fume hood at room temperature. The free-standing electrolyte films were dried in a vacuum oven for 24 hours at 40 °C. The samples were stored in a desiccator until further use.

2.2. Characterization

The conductivity was determined by impedance spectroscopy using high frequency resonance analyzer (HFRA) model 1255 with applied frequency from 1 MHz to 0.1 Hz at 100 mV amplitude. The 16 mm diameter sample of disc shape was sandwiched between the two stainless steel blocking electrodes. The ionic conductivity was measured at room temperature and at temperature range of 303 K to 373 K. The conductivity (σ) was calculated from the bulk resistance (R_b) obtained from the intercept of real impedance axis, film thickness (t), and the product of effective contact area (A) according to the equation $\sigma = [t/(AR_b)]$. Fourier transforms infrared (ATR-FTIR) analysis was carried out using 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 employed to analyze the crystalline and amorphous structural behaviour of the electrolyte. The data was taken at the diffraction angle 2θ from 10° to 80° at the rate of 0.025 $^\circ\text{s}^{-1}$. The morphology of polymer electrolyte was examined by scanning electron microscopy (SEM) Philip XL 30 model with magnifications of 1000 \times .

3. RESULT AND DISCUSSION

3.1. Ionic conductivity

According to the impedance spectra shown in Fig. 1, two regions were observed; semicircle portion in the high frequency range which is mainly the result of ions conduction [13,14,15] and the linear region in the low frequency which is related to the bulk effect of blocking electrodes [13,16,17].

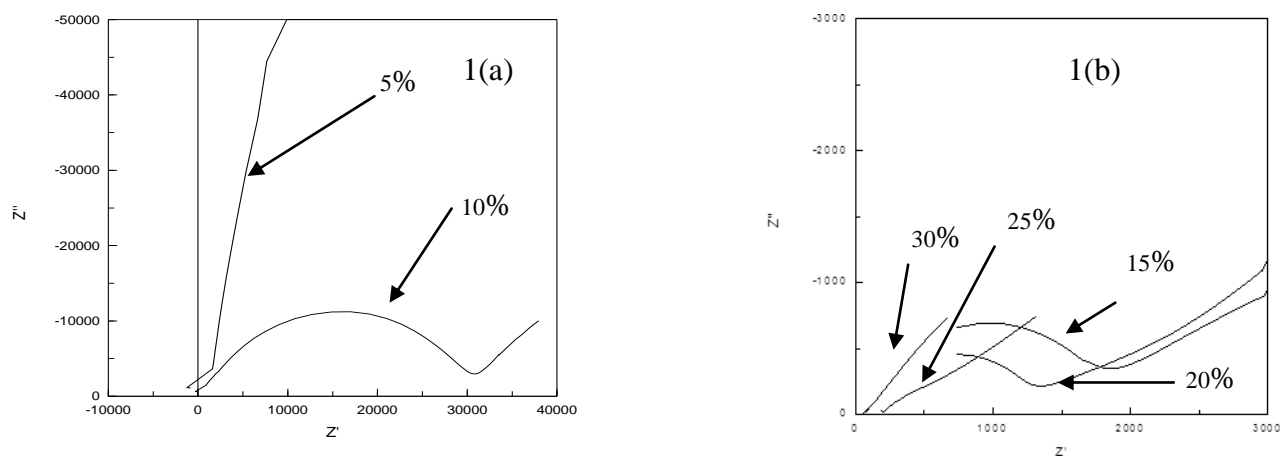


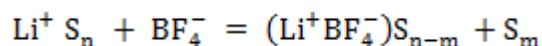
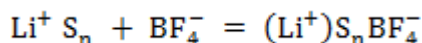
Figure 1. AC impedance plot of (a) PVDF-HFP/MG49/LiBF₄ (5-10 wt. %) (b) 15-30 wt. % LiBF₄

The room temperature conductivity for PVDF-HFP/MG49 electrolyte with various percentage of LiBF₄ salt and the [O/Li] ratio of PVDF-HFP/MG49/ LiBF₄ polymer electrolyte are presented in Table 1.

Table 1. Ionic conductivity and [O/Li] ratio of PVDF-HFP/MG49/LiBF₄

wt. % salt	Conductivity (S cm ⁻¹)	O/Li ratio
5	5.0×10^{-9}	19/1
10	4.9×10^{-7}	10/1
15	6.8×10^{-6}	7/1
20	9.8×10^{-6}	5/1
25	6.3×10^{-5}	4/1
30	2.8×10^{-4}	4/1
35	6.7×10^{-6}	3/1

The impedance spectra for PVDF-HFP/MG49 with 5-10 wt. % LiBF₄ are shown in Fig. 1(a) and for 15-30 wt% LiBF₄ are shown in Fig. 1 (b). The lowest conductivity value of PVDF-HFP/MG49/LiBF₄ system was 5.03×10^{-9} S cm⁻¹ at 5 wt.% LiBF₄ and the highest ionic conductivity was 2.32×10^{-4} S cm⁻¹ at 30 wt. % LiBF₄. The ionic conductivity has increased significantly with the concentration of LiBF₄ salt as shown in Fig 2. This is due to the increase in the number of charge carriers in the blend [1,2,14,18,19]. Two types of ion pairs exist at high content of salt which can be described by the following equations [19],



,where S represents the solvating species. Increasing the number of free ions is due to long-range coulombic forces lead to re-dissociation of these ions. Short-range ion-solvent interaction takes place at higher concentration so that the number of ions dissolved in the electrolyte medium increases and the effective number of charged species decreases [21]. The blending of MG49 into PVDF-HFP matrix decreases the crystallinity of polymer and increases the degree of amorphicity of PVDF-HFP/MG49 polymer electrolyte [23]. According to the previous studies reported by [18,23,24,25], there is a coordinate bond between Li⁺ ions and oxygen atoms in the polymer salt complex. [O/Li]

ratio for the optimum LiBF_4 salt loading is 4 of oxygen atoms to 1 lithium ion (4:1). Different value in $[\text{O}/\text{Li}]$ indicates to difference in weight percent (wt. %) lithium salt. The higher ionic conductivity with the addition of 30 wt. % LiBF_4 is due to the low lattice energy (699 KJ/mol) of LiBF_4 , hence easier solvation of Li ions by the polymer host [8].

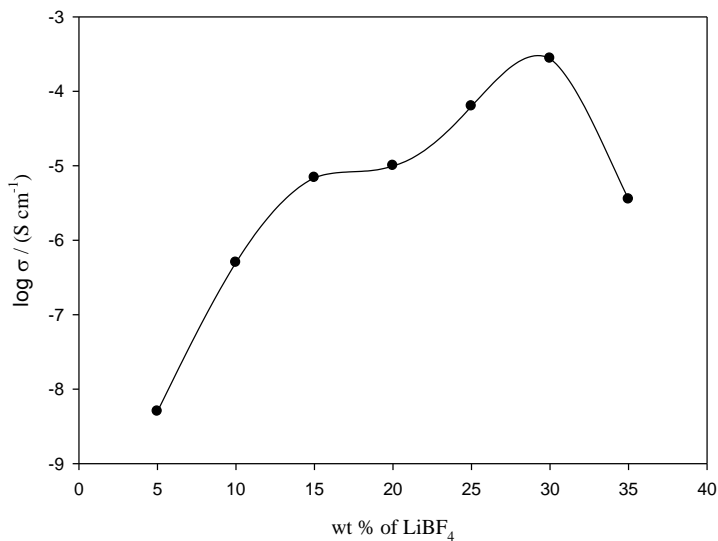


Figure 2. Variation of ionic conductivity with concentration of LiBF_4 salt

Fig. 3 shows the temperature dependence of the ionic conductivity of the PVDF-HFP/MG49 electrolyte containing of 30 wt. % LiBF_4 by Arrhenius model.

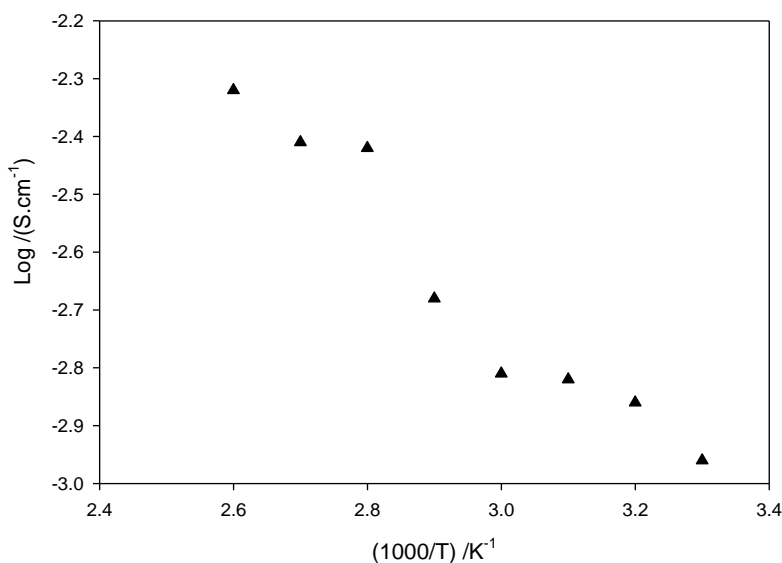


Figure 3. Arrhenius plot of (70:30) PVDF-HFP/MG49 electrolyte at 30 wt. % LiBF_4

The relationship is non-linear since the linear correlation factor is less than 0.99 indicating the electrolyte does not obey the Arrhenius rule. Therefore, the pre-exponential factor, σ_0 and activation energy, E_a of the electrolyte cannot be estimated from the plot. It is clearly observed that by increasing the temperature, the ionic conductivity increases which is in good agreement with the theory by Armand [26]. This is rationalized by identifying the free volume model [27]. In the present investigation, the highest conductivity is $4.8 \times 10^{-3} \text{ S cm}^{-1}$ at 373 K. The increase in conductivity with temperature can be linked to the decrease in viscosity and, hence, increases the chain flexibility of the electrolyte. As the temperature increases, the mobility and the dissociation rate of Li ions also increase, thus improving the conductivity of the electrolyte [28,29]. As temperature increases, the polymer expands and produced empty areas that cause species such as polymer segments, motion ions or solvated molecules to move into these free volumes. The segmental movement of polymer promotes the transfer of ionic motion by allowing the ions to transfer from one site to another in the same polymer chain or to the neighboring polymer chain resulting to the increment of ionic conductivity [6].

3.2. FTIR

Fig. 4 shows the IR spectra of the PVdF-HFP, MG49 and PVDF-HFP/MG49 blend. The spectrum of PVDF-HFP shows the peak at 974 cm^{-1} corresponding to the α phase crystals and the peak at 838 cm^{-1} is assigned to β phase [6,8].

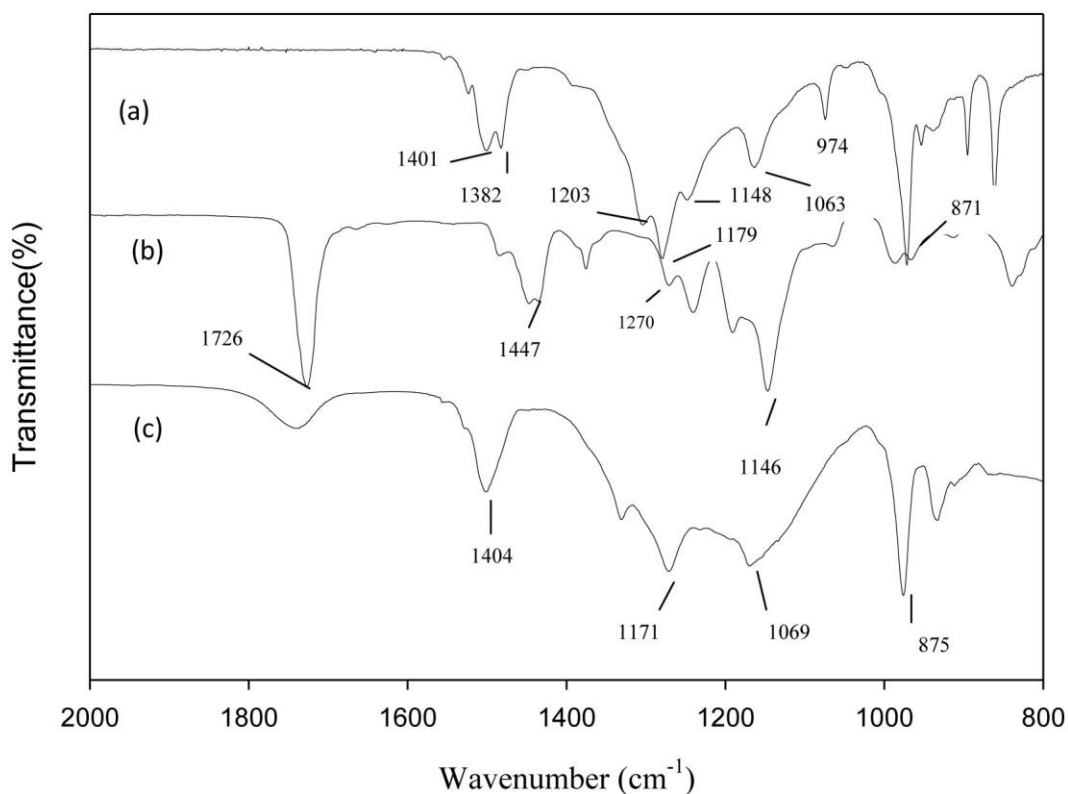


Figure 4. FTIR spectra of (a) PVDF-HFP, (b) MG49, (c) PVDF-HFP/MG49 blend

Detected peaks for crystalline phase disappear in PVDF-HFP/MG49 blend indicating that the crystallinity of PVDF-HFP is reduced by blending. The amorphous phase of PVDF-HFP is observed at 871 cm^{-1} which is shifted to 875 cm^{-1} in the blend. The band around 1063 cm^{-1} corresponds to symmetrical stretching mode of CF_2 which is shifted to 1069 cm^{-1} in the blend. Detected peaks at 1148, 1203, 1179 and 1382 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 CH_2 wagging, respectively in the pure polymer [30,31, 32] disappear in the blend. The absence of the peaks in the blend indicates that two polymers are well-mixed and there is no phase separation.

The strong and sharp peak of $\text{C}=\text{O}$ stretching mode of PMMA appear at 1726 cm^{-1} in pure MG49 is absent in the blend. The identified peaks at 1146, 1270 and 1447 cm^{-1} correspond to the C-O-C asymmetric, C-O symmetric and O- CH_3 in pure MG49 [10,11,13,23] are also absent in the blend. As evident in Fig. 4, upon the addition of LiBF_4 , the observed peaks at 875, 1069 and 1171 cm^{-1} in the blend of PVDF-HFP/MG49 shifted to higher frequency, 877, 1070, 1172 cm^{-1} , respectively in the complex. After the salt addition, the ester functional group ($\text{C}=\text{O}$) in PMMA appears at 1726 cm^{-1} . The intensity of the peak reduces which confirms the interaction between Li ions and oxygen atoms in the structure of polymer, leads to the formation of polymer complex [9,12]. The deformed vibration of CH_2 groups appears at the frequency of 1401 cm^{-1} , shifting to high position (1404 cm^{-1}) due to the weak interaction between H atoms of CH_2 groups and F atoms of CF_2 groups [30,31,33,34].

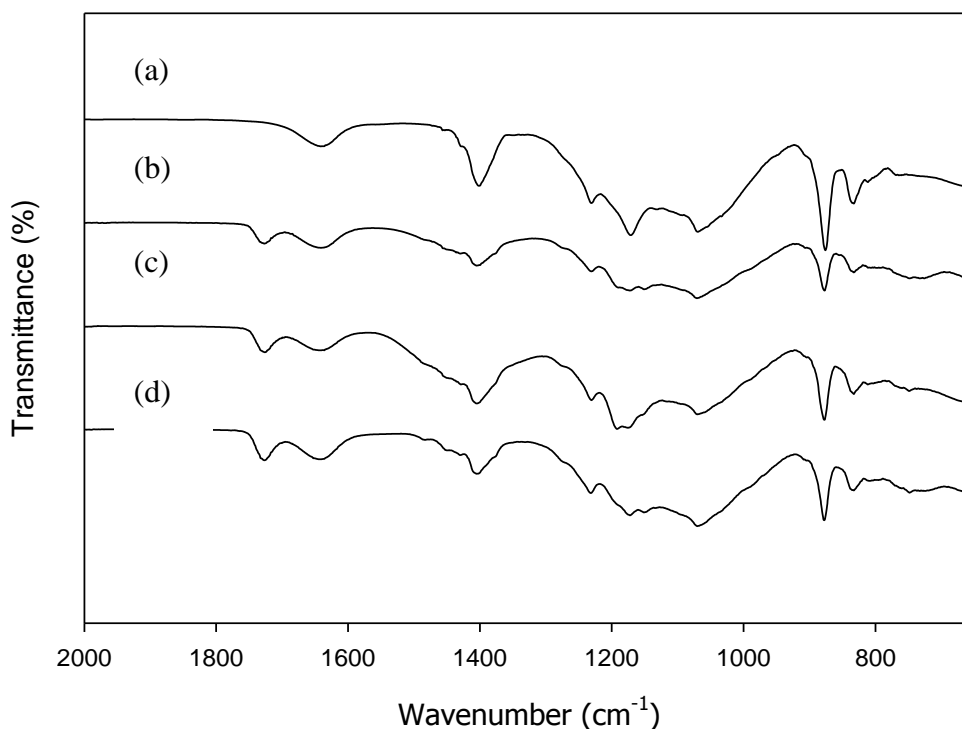


Figure 5. FTIR spectrums of (a) PVDF-HFP/MG49 blend, (b) 10 wt% LiBF_4 (c) 20 wt% LiBF_4 (d) 30 wt% LiBF_4

3.3. XRD

Fig. 6 shows the XRD patterns of LiBF_4 , pure PVDF-HFP, pure MG49, and PVDF-HFP- MG49-LiBF_4 . The peaks at diffraction angle of 14° , 21° , 23° , 26° , 28° , 32° , 39° , 44° and 55° were observed in the LiBF_4 salt XRD pattern [10].

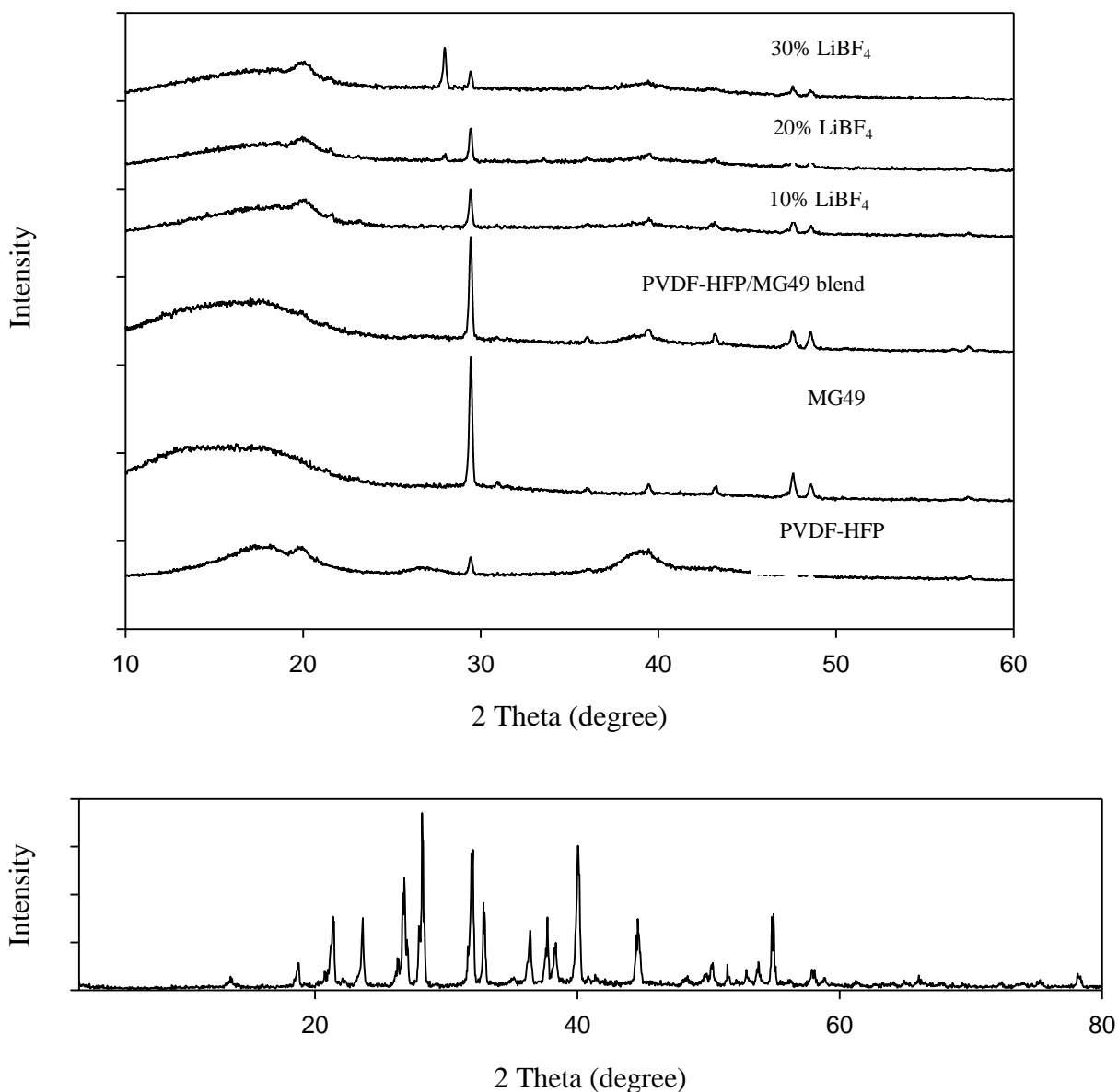


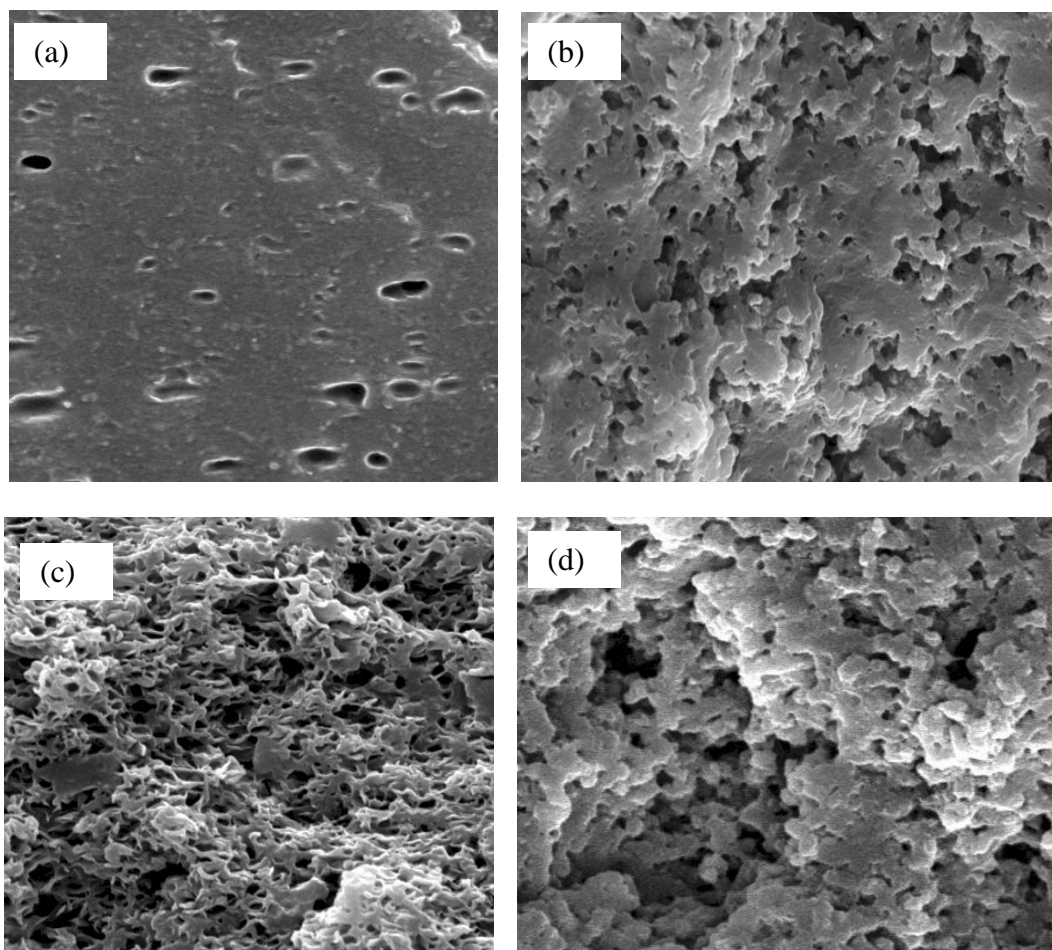
Figure 6. XRD spectra of LiBF_4 , PVDF-HFP, MG49, PVDF-HFP/MG49 blend with various percentage of LiBF_4

The XRD spectrum for pure PVDF-HFP, exhibits peaks at $2\theta = 18^\circ$, 20° and 26° which illustrate the partial crystalline nature of PVDF-HFP polymer [1,8,34,35]. In the XRD scan of pure MG49, it can be observed that the hump in the region between 10° to 23° and the single peak with high intensity at $\theta = 29^\circ$ attributed to MMA monomer which demonstrate the semi crystalline nature of

MG49 [10,36]. It was found that the crystallinity degree of polymer decreases by blending two polymers and upon the addition of salt, there was a significant decrease in the crystallinity degree of polymer up to 10 % wt. salt by changing in the intensity of MMA monomer peak and broadening of polymer hump. As reported in [10,13,35,37], it was found that at high content of salt, re-crystallization of lithium salts occurred which is due to the formation of ion pairs between Li^+ and BF_4^- .

3.4. Morphological studies

Pure MG rubber in Fig. 7(a) shows a rough surface and micro-pore structure which is an evident for interaction between the solvent and polymer matrix [38]. The porous nature of the PVDF-HFP is clearly observed in Fig. 7(b) [20]. As evident from Fig. 7(c), upon blending, the pore size becomes smaller and no phase separation was observed which indicates that the blend is compatible. For the blend doped with the salt (Fig. 7d and 7e), the number of micro-pores decreases and the size of pores decreases as well. The amorphousness degree of blend rises, hence the ionic conductivity increases. As described in the XRD analysis, re-crystallization occurred at high amount of salt (30 wt. %) due to the distribution of LiBF_4 salt on the surface of polymer.



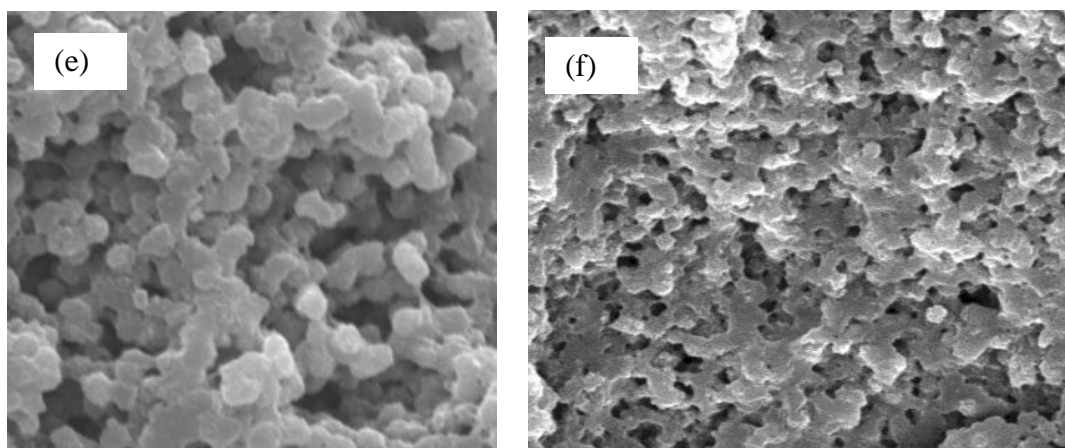


Figure 7. SEM micrographs (1000 \times) of (a) Pure MG49 (b) Pure PVDF-HFP (c) PVDF-HFP/MG49 blend (d) 10 wt.% LiBF₄ (e) 20 wt.% LiBF₄ (f) 30 wt.% LiBF₄

4. CONCLUSIONS

Solid polymer electrolyte PVDF-HFP/MG49 doped with LiBF₄ salt has been successfully prepared by solution casting technique. The ionic conductivity was significantly improved from 10^{-9} to 10^{-4} S cm⁻¹ with the increase in percentage of LiBF₄ salt. The highest ionic conductivity was at 2.8×10^{-4} S cm⁻¹ for the sample with 30 wt. % of LiBF₄. FTIR analysis confirms the interaction between the Li ions and polymer. X-ray diffraction confirms that by introducing LiBF₄ salt, the crystallinity degree decreases. Morphology study showed that the compatibility of blend and amorphous phase increase by addition of salt which lead to the increase in ionic conductivity.

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