

Proton Conducting Polymer Electrolytes Based on PVDF-HFP and PVDF-HFP/PEMA Blend

(Elektrolit Polimer Pengkonduksi Proton berasaskan PVDF-HFP dan Adunan PVDF-HFP/PEMA)

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ABSTRACT

In the present work, polymer electrolytes of poly(vinylidene fluoride co-hexafluoropropylene) (PVDF-HFP) and PVDF-HFP/poly(ethyl methacrylate) (PVDF-HFP/PEMA) blend complexed with different concentrations of ammonium triflate ($\text{NH}_4\text{CF}_3\text{SO}_3$) were prepared and characterized. The structural and thermal properties of the electrolytes were studied by XRD and DSC while the electrical properties were investigated by impedance spectroscopy. Ionic transference number measurements were done by D.C polarization technique. The results of these study showed that the PVDF-HFP/PEMA based electrolytes exhibit higher ionic conductivity as compared to PVDF-HFP based electrolytes. This could be attributed to the higher degree of amorphicity in the PVDF-HFP/PEMA based electrolytes. The results of ionic transference number measurements showed that the charge transport in these electrolytes was mainly due to ions and only negligible contribution comes from electrons.

Keywords: Amorphicity; ionic conductor; polymer blend; structural properties; thermal properties

ABSTRAK

Dalam penyelidikan ini, elektrolit polimer poli(vinilidin florida ko-heksafloropropilin) (PVDF-HFP) dan campuran PVDF-HFP/poli(etil metakrilat) (PEMA) dengan kepekatan amonium triflat yang berbeza telah disediakan dan dicirikan. Sifat-sifat struktur and terma elektrolit telah dikaji menggunakan pembelauan sinar-X dan analisis pengimbas kalorimetri sementara sifat elektrik diukur menggunakan spektroskopi impedans. Pengukuran nombor pemindahan ion telah dilakukan menggunakan teknik pengutuban A.T. Kajian menunjukkan bahawa elektrolit berasaskan PVDF-HFP/PEMA mempunyai kekonduksian ion yang lebih tinggi berbanding elektrolit berasaskan PVDF-HFP. Ini disebabkan oleh darjah amorfus yang lebih tinggi di dalam elektrolit berasaskan PVDF-HFP/PEMA. Keputusan pengukuran nombor pemindahan ion menunjukkan bahawa pengangkutan cas di dalam sistem ini disebabkan oleh ion-ion dengan sedikit sumbangan daripada elektron.

Kata kunci: Amorfus; campuran polimer; konduktor ionik; sifat struktur; sifat terma

INTRODUCTION

PVDF-HFP is a prominent polymer known for its favorable characteristics. This copolymer has been shown to be a promising matrix for an electrolyte material. It has a high dielectric constant of $\epsilon = 8.4$ which can assist in greater dissociation of salt. It also comprises of both amorphous and crystalline phases. The amorphous phase of this copolymer assists higher ionic conduction whereas the crystalline phase acts as a mechanical support (Jeon et al. 2006; Kim et al. 2006; Vijayakumar et al. 2008).

Most of the studies reported in the literature employed PVDF-HFP for development of Li ion conducting electrolytes (Aravindan et al. 2009; Fan et al. 2002; Saikia & Kumar 2004; Saikia et al. 2008). Only limited number of proton conducting electrolyte systems based on PVDF-HFP have been reported. Missan et al. (2006) reported that the conductivity of proton conducting PVDF-HFP complexed with oxalic acid increased by four orders of magnitude with the addition of DMA and the maximum

conductivity achieved was $1.2 \times 10^{-4} \text{ S cm}^{-1}$. Singh and Sekhon (2003) reported the conductivity behavior of proton conducting systems based on PVDF-HFP. According to these authors, the PVDF-HFP doped with benzoic acids exhibited room temperature conductivity of $0.42 \times 10^{-4} \text{ S cm}^{-1}$. Other study on proton conducting system using PVDF-HFP has been done by Choi et al. (2004). They found that the conductivity of 15PVDF-HFP-70PC-15H₃PO₄ was $2.1 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature. All the above mentioned proton conducting systems used inorganic acids as dopants.

According to Hema et al. (2008), proton conducting polymer electrolytes containing inorganic acids suffer from chemical degradation and mechanical integrity and thus are unsuitable for practical applications. Therefore for the present work, $\text{NH}_4\text{CF}_3\text{SO}_3$ was used as doping salt since ammonium salts are also good proton donors to polymer matrix (Hema et al. 2008). In this study, two proton conducting polymer electrolyte systems were prepared

using PVDF-HFP and PVDF-HFP/PEMA blend as the hosts. The characteristics of the prepared proton conducting systems have been characterized and compared.

MATERIALS AND METHOD

PREPARATION

In this study, all proton conducting polymer films containing PVDF-HFP doped with $\text{NH}_4\text{CF}_3\text{SO}_3$ have been prepared by solution casting technique. PVDF-HFP ($M_w \sim 400000$) and $\text{NH}_4\text{CF}_3\text{SO}_3$ (99%) were obtained from Aldrich. A desired amount of PVDF-HFP was dissolved in DMF at 40°C using magnetic stirrer. After 1h of stirring, these solutions were added with appropriate amount of $\text{NH}_4\text{CF}_3\text{SO}_3$ and stirred at room temperature for 24 h. The homogeneous solutions were then poured into Petri dishes and left to dry for a few days to form films at room temperature. In order to prepare the polymer blend based electrolytes, PVDF-HFP ($M_w \sim 400,000$) and PEMA ($M_w \sim 515,000$) of wt% ratio of 85:15 were first dissolved in DMF at 40°C before appropriate amounts of $\text{NH}_4\text{CF}_3\text{SO}_3$ were added.

CHARACTERIZATION

In order to study structural features and the occurrence of complexation in the polymer systems studied in this work, X-ray diffraction analysis was carried out. The XRD patterns of the polymer system were recorded using the Bruker D8 Advanced X-ray diffractometer. The thermal properties and degree of crystallinity of the systems were investigated using DSC METTLER TOLEDO DSC822 under argon inert condition. Each sample was sealed in an aluminum crucible and heated from -60 to 200°C . The ionic conductivity of the polymer electrolytes was determined by AC impedance spectroscopy technique using HIOKI 3528-50 LCR Hi Tester. Each sample was placed between stainless steel electrodes and impedance measurement was done in the frequency range of 42 Hz to 5 MHz at various temperatures. The ionic transference number (t_{ion}) of the highest conducting PVDF-HFP and PVDF-HFP/PEMA based electrolyte systems was evaluated by the DC polarization technique. In this technique, the carbon/polymer electrolyte/carbon cell was polarized by applying a potential of 1.0 V and the current was monitored.

RESULTS AND DISCUSSION

X-RAY DIFFRACTION STUDIES

Figure 1 illustrates the XRD patterns of $\text{NH}_4\text{CF}_3\text{SO}_3$, PVDF-HFP and PVDF-HFP/PEMA based electrolyte systems. The XRD pattern of PVDF-HFP exhibits peaks at $2\theta = 19^\circ$ and 21° corresponding to the semicrystalline nature of the polymer (Saikia & Kumar 2004). The XRD pattern of PVDF-HFP/PEMA (Figure 1(c)) also exhibits the same peaks but of lower relative intensity. This may be due to the lower crystalline fraction in the system. This effect

arises with the addition of PEMA which reduces the long range order of PVDF-HFP. From Figure 1(b) and 1(c), it can be observed that the two PVDF peaks become a single broad peak upon addition of $\text{NH}_4\text{CF}_3\text{SO}_3$. This indicates that complexation has occurred between the hosts and the doping salt. This also showed that the $\text{NH}_4\text{CF}_3\text{SO}_3$ has disrupted the crystalline region in the PVDF-HFP and PVDF-HFP/PEMA blend system. The absence of the peaks of $\text{NH}_4\text{CF}_3\text{SO}_3$ (Figure 1(a) and 1(b)) indicates complete complexation of the salt in host polymer matrices and the salt does not remain as a separate phase in the electrolyte systems.

DSC STUDIES

Thermal analysis using DSC was performed in order to observe change in melting temperature and degree of crystallinity that may be caused by blending of PEMA and addition of $\text{NH}_4\text{CF}_3\text{SO}_3$ to PVDF-HFP. The relative degree of crystallinity of the polymer electrolytes was estimated using the equation,

$$X_c = \frac{\Delta H_m}{\Delta H_o} \times 100\% \quad (1)$$

where ΔH_m is the enthalpy of fusion for the polymer electrolytes. ΔH_{mo} is 104.7 J g^{-1} which is the enthalpy of fusion for 100% crystalline PVDF-HFP (Cao et al. 2006). Figure 2 shows the DSC curves for PVDF-HFP and PVDF-HFP/PEMA based electrolyte systems investigated in this work. The endothermic peaks around $130 - 150^\circ\text{C}$ correspond to the melting point of PVDF-HFP and PVDF-HFP/PEMA blend based polymer electrolytes. The values of the melting temperature, enthalpy of fusion and relative degree of crystallinity of PVDF-HFP and PVDF-HFP/PEMA based electrolytes are listed in Table 1. The table reveals that the melting point and relative degree of crystallinity of PVDF-HFP/PEMA is lower than those of the PVDF-HFP. This indicates that the PVDF-HFP/PEMA blend electrolyte system is more amorphous compared to the PVDF-HFP system. This was due to the presence of PEMA which reduces the long range order of PVDF-HFP. This observation is consistent with the XRD result. Table 1 also reveals that the relative degree of crystallinity of the PVDF-HFP and PVDF-HFP/PEMA based electrolytes decreases with the increase in $\text{NH}_4\text{CF}_3\text{SO}_3$ salt concentration. This means that the increase in salt concentration leads to an increase in the amorphous phase. This amorphous phase makes the electrolytes more flexible resulting in an increase in segmental motion of the polymer which favors high ionic conduction (Noor et al. 2010).

CONDUCTIVITY STUDIES

Table 2 shows the room temperature conductivity for PVDF-HFP and PVDF-HFP/PEMA blend based electrolyte systems with various concentrations of $\text{NH}_4\text{CF}_3\text{SO}_3$. The conductivity of both systems is observed to increase with

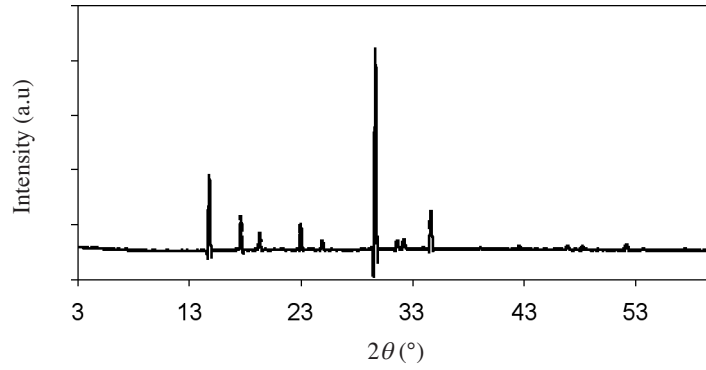


FIGURE 1(a). XRD pattern of $\text{NH}_4\text{CF}_3\text{SO}_3$

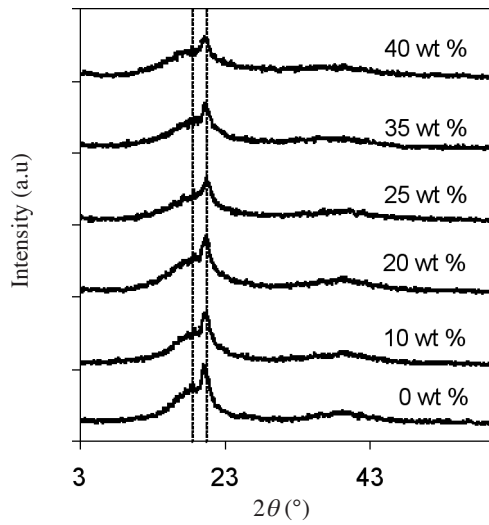


FIGURE 1(b). XRD patterns of PVDF-HFP with 0, 10, 20, 25, 35 and 40 wt% of $\text{NH}_4\text{CF}_3\text{SO}_3$

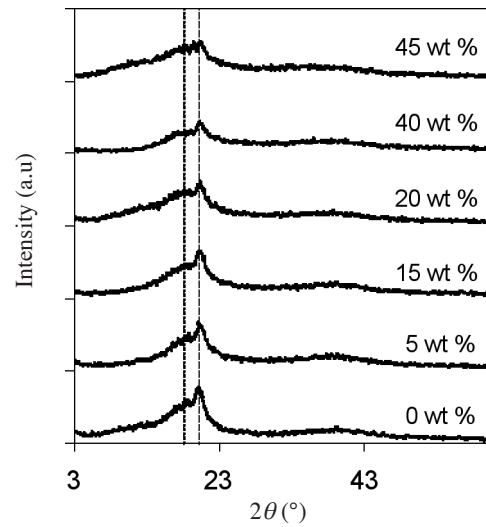


FIGURE 1(c). XRD patterns of PVDF-HFP/PEMA with 0, 5, 15, 20, 40 and 45 wt% of $\text{NH}_4\text{CF}_3\text{SO}_3$

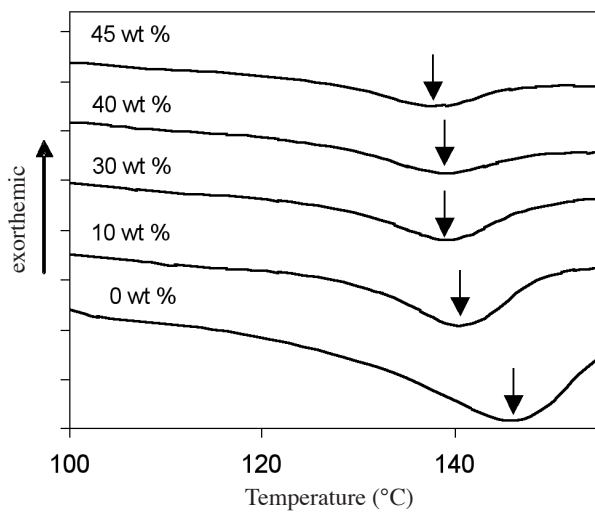


FIGURE 2(a). DSC curves of PVDF-HFP with 0, 10, 20, 30 and 40 wt% of $\text{NH}_4\text{CF}_3\text{SO}_3$

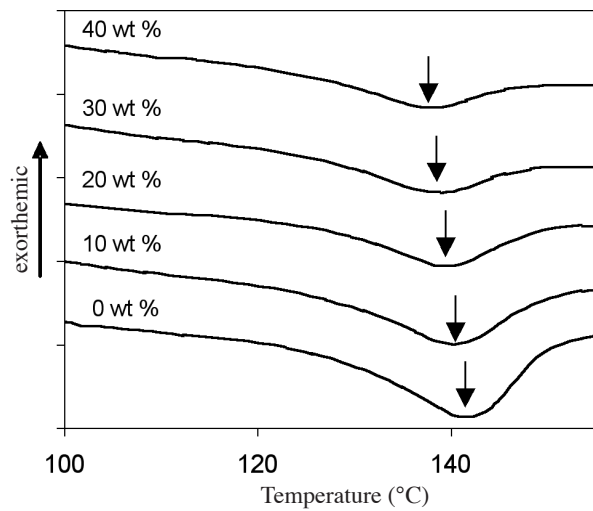


FIGURE 2(b). DSC curves of PVDF-HFP/PEMA with 0, 10, 20, 30 and 40 wt% of $\text{NH}_4\text{CF}_3\text{SO}_3$

increasing salt concentration from $\sim 10^{-11}$ S cm^{-1} to $\sim 10^{-4}$ S cm^{-1} . The increase in conductivity with increasing salt concentration can be associated to an increase in the number of mobile ions (Ramya et al. 2007) and enhancement of amorphous region as shown by XRD and DSC studies. The conductivity for both blended and unblended PVDF-HFP systems decreases slightly upon addition of 45 wt % of $\text{NH}_4\text{CF}_3\text{SO}_3$. This can be attributed to ionic association and reduced dissociation of salt which result in a decrease in the number of mobile ions (Ahmad et al. 2010). Table 2 also shows that at each salt concentration, the PVDF-HFP/PEMA based electrolyte exhibits higher conductivity compared to the PVDF-HFP based electrolyte. This may be attributed to the higher degree of amorphicity of PVDF-HFP/PEMA based electrolytes. The highest conductivity for PVDF-HFP based electrolyte system is 5.43×10^{-4} S cm^{-1} for the film containing 40 wt% of $\text{NH}_4\text{CF}_3\text{SO}_3$ while the highest conductivity for the PVDF-HFP/PEMA blend

electrolyte system is 7.07×10^{-4} S cm^{-1} for the film with 40 wt% $\text{NH}_4\text{CF}_3\text{SO}_3$.

IONIC TRANSFERENCE NUMBERS

The ionic transference number for the highest conducting PVDF-HFP and PVDF-HFP/PEMA based electrolytes was determined by the D.C polarization technique. The value of t_{ion} was calculated from the polarization current versus time plot using the equation:

$$t_{\text{ion}} = \frac{i_r - i_e}{i_r} \quad (2)$$

where i_T and i_e are the total and residual current respectively. Figure 3 depicts the plots of the polarization current versus time for the electrolyte films. The ionic transference number of both electrolyte systems was found to be ~ 0.95 . This suggests that the conductivity of PVDF-HFP and

TABLE 1. Melting point, enthalpy of fusion and degree of crystallinity values of PVDF-HFP and PVDF-HFP/PEMA based electrolytes

Composition (wt% ratio)	T_m ($^{\circ}\text{C}$)	ΔH_m (J g^{-1})	X_c (%)
PVDF-HFP: $\text{NH}_4\text{CF}_3\text{SO}_3$			
100:0	146.0	30.4	29.0
90:10	140.4	15.24	14.55
80:20	140.1	7.89	7.53
60:40	138.4	5.38	5.14
55:45	137.6	5.83	5.57
PVDF-HFP/PEMA: $\text{NH}_4\text{CF}_3\text{SO}_3$			
100:0	141.4	10.84	10.35
90:10	140.4	8.02	7.66
80:20	139.3	5.80	5.54
70:30	138.1	4.75	4.54
60:40	137.5	3.44	3.29

TABLE 2. Room temperature conductivity values of PVDF-HFP and PVDF-HFP/PEMA based electrolytes

Composition (wt% ratio)	Conductivity at room temperature (S cm^{-1})	
	Polymer: $\text{NH}_4\text{CF}_3\text{SO}_3$	PVDF-HFP/PEMA based electrolyte
100:0	1.46×10^{-11}	2.97×10^{-11}
95:5	6.76×10^{-9}	8.00×10^{-9}
90:10	6.12×10^{-7}	2.05×10^{-6}
85:15	3.82×10^{-6}	1.77×10^{-5}
80:20	6.54×10^{-6}	3.01×10^{-5}
75:25	3.09×10^{-5}	4.24×10^{-5}
70:30	2.87×10^{-4}	3.21×10^{-4}
65:35	3.48×10^{-4}	4.01×10^{-4}
60:40	5.43×10^{-4}	7.07×10^{-4}
55:45	2.31×10^{-6}	5.95×10^{-4}
50:50	Mechanically unstable	Mechanically unstable

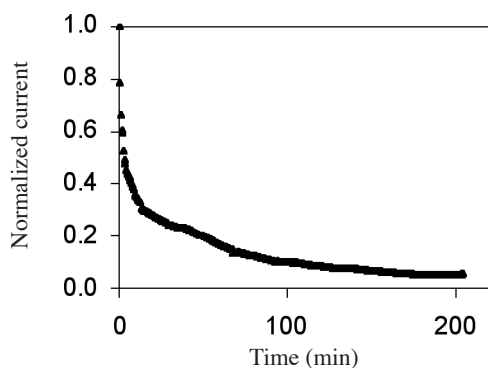


FIGURE 3(a). Current-time curve of PVDF-HFP containing 40 wt% of $\text{NH}_4\text{CF}_3\text{SO}_3$

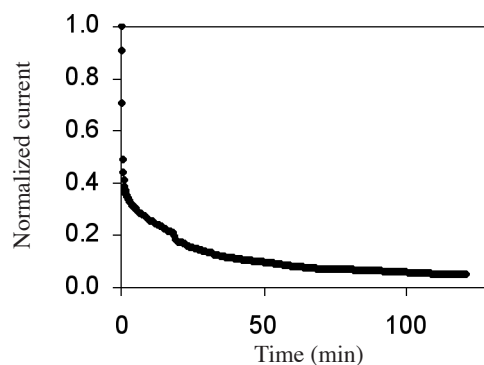


FIGURE 3(b). Current-time curve of PVDF-HFP/PEMA containing 40 wt% of $\text{NH}_4\text{CF}_3\text{SO}_3$

PVDF-HFP/PEMA based electrolytes was predominantly due to ions and only negligible contribution came from electron (Baskaran et al. 2004).

CONCLUSION

From the present comparative study of PVDF-HFP and PVDF-HFP/PEMA based electrolytes, it can be concluded that both PVDF-HFP and PVDF-HFP/PEMA form complexes with $\text{NH}_4\text{CF}_3\text{SO}_3$ salt as confirmed by XRD study. The maximum conductivity for PVDF-HFP based electrolytes was found to be $5.43 \times 10^{-4} \text{ S cm}^{-1}$ whereas for the PVDF-HFP/PEMA based electrolyte was $7.07 \times 10^{-4} \text{ S cm}^{-1}$. The higher conductivity observed in the PVDF-HFP/PEMA based electrolytes could be attributed to the higher degree of amorphicity. Total ionic transport number for the PVDF-HFP and PVDF-HFP/PEMA based electrolyte indicates that the charge carriers in the electrolytes are dominated by ions. This showed that the electrolytes are ionic conductors.

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