

CHAPTER 5

RESULTS OF XRD STUDIES

5.1 Introduction

In this chapter the x-ray diffraction results of the PVDF-HFP based electrolytes with NaI and KI salts as well as the corresponding plasticized systems will be presented. X-ray diffraction (XRD) investigations were carried out to study the extent to which the electrolyte systems are amorphous or crystalline. The increase or decrease in amorphousness is important since such nature of the electrolytes affect their conductivity.

5.2 XRD Studies on NaI Containing Electrolytes

5.2.1 XRD Diffractogram for (PVDF-HFP) and (PVDF-HFP)-NaI Electrolytes.

X-ray diffractograms shown in Fig. 5.1 (a) to (f) include that of pure (PVDF-HFP) and (PVDF-HFP)-NaI polymer electrolytes with different NaI concentrations ranging from 10 to 50 wt.%. The diffractogram of pure PVDF-HFP in Fig. 5.1 (a) shows characteristic peaks at $2\theta = 18.2^\circ$, 20.1° , 26.5° and 38.3° . According to Li et al., (2005) and Stolarska et al., (2007), peaks at $2\theta = 18.2^\circ$, 20° , 26.6° and 38° correspond to the crystalline peaks of PVDF. This indicates that, the co-polymer PVDF-HFP corresponds well with crystalline PVDF in spite of having HFP amorphous regions.

Fig. 5.1: X-ray diffraction patterns of (a) Pure PVDF-HFP and (PVDF-HFP)-NaI electrolytes with various contents of NaI (in wt.%); (b) 10 (c) 20 (d) 30 (e) 40 and (f) 50

Fig. 5.1, (b) – (f) show the the diffractograms of polymer-salt complexes. The intensity of the crystalline peak at $2\theta = 18.2^\circ$ decreases with the increase of NaI content. The peak

at $2\theta = 26.5^\circ$ almost disappears and those at $2\theta = 20.1^\circ$ and 38.3° undergo changes as the NaI content in the electrolyte increases. The intensity reduction at $2\theta = 18.2^\circ$ and elimination of peak at $2\theta = 26.5^\circ$ indicate the decrease in crystallinity or increase in amorphousness of PVDF-HFP upon addition of NaI salt. In order to quantify the amorphousness or crystallinity of the electrolytes, the diffractograms were deconvoluted using the Origin 8.0 software. The deconvolution analysis and results for (PVDF-HFP)-NaI are given in section 5.2.2.

5.2.2 Deconvolution of (PVDF-HFP) and (PVDF-HFP)-NaI X-ray Diffractograms

The deconvolution of X-ray diffractograms was carried out in the range $2\theta = 5^\circ$ to 55° . The deconvoluted diffractogram for pure PVDF-HFP is presented in Fig. 5.2. From the figure, the crystalline peaks of pure PVDF-HFP can be seen at $2\theta = 18.21^\circ$, 20.05° , 26.15° and 38.63° . The degree of crystallinity was calculated using the equation (Hodge et al., 1996):

$$X_C = (I_C / I_T) \times 100\% \quad (5.1)$$

where I_C is area under the crystalline peaks at $2\theta = 18.21^\circ$, 20.05° , 26.15° and 38.63° . I_T is the total area under the diffractogram from $2\theta = 5^\circ$ to 55° . Detail results for the deconvoluted diffractogram obtained from the Origin 8.0 software and degree of crystallinity calculated for PVDF-HFP are presented in Table 5.1. From these calculations, the degree of crystallinity for pure PVDF-HFP is found to be 78.4%.

Fig. 5.2: Deconvoluted XRD diffractogram for pure PVDF-HFP

From the figure, the actual crystalline peaks as reported in the literature have shown broadening which indicates that the samples has become more amorphous. However, in the calculation for d.o.c. these peaks are still considered the crystalline peaks.

Table 5.1: Degree of crystallinity for PVDF-HFP sample (without salt)

Peaks	Peak's center	Area (a.u.)
1	11.48	433.1
2	18.21	1104.9
3	20.05	67.9
4	26.15	676.5
5	32.63	134.6
6	38.63	725.3
7	44.17	143.5
Total Area (I_T)		3285.8
Total crystalline peak's area (I_C)		2574.6
Degree of crystallinity (X_C) (%)		78.40

Fig. 5.3 (a) to (e) show the deconvoluted diffractograms for different NaI concentrations ranging from 10 to 50 wt.%. The percentage degree of crystallinity (X_C) calculated for different salt concentrations are listed in Table 5.2. Previously, from Table 5.1, it can be seen that the degree of crystallinity for pure PVDF-HFP is 78.4%. Upon addition of 10 wt.% NaI, the value starts to decrease to 45.6% and reaches the lowest value at 34.9% for the sample with 40 wt.% NaI. The value increases again after addition of 50 wt.% NaI. The decrease in the degree of crystallinity (d.o.c) indicates the increase in the amorphousness of the sample up to 40 wt.% NaI.

Fig. 5.3: Deconvoluted X-ray diffractograms of (PVDF-HFP)-NaI electrolyte having different NaI content in wt.%, (a) 10, (b) 20 (c) 30, (d) 40 and (e) 50

Table 5.2 lists the total area of crystalline peaks and the total area under the diffractogram for each sample together with the degree of crystallinity.

Table 5.2: Degree of crystallinity (d.o.c) for (PVDF-HFP)-NaI polymer electrolytes having different NaI contents

5.2.3 X-ray Diffractograms for (PVDF-HFP)-NaI-(EC/PC) Electrolytes

Fig. 5.4 (b) to (f) display the X-ray diffractograms for (PVDF-HFP) – NaI – EC/PC plasticized electrolytes with various EC/PC content ranging from 0 to 50 wt.%. In all electrolytes the ratio of EC:PC was maintained at 1:1. It is clearly seen that the crystalline peak at $2\theta = 18.2^\circ$ has merged with that at $2\theta = 20.1^\circ$ and slightly shifted to the right to $2\theta = 20.27^\circ$ as the EC/PC content is increased. The crystalline peak at $2\theta = 26.5^\circ$ has disappeared and the peak at $2\theta = 38.3^\circ$ has shifted to the higher 2θ angle around 39.0° to 40.0° . The elimination of the crystalline peak indicates the decrease in crystallinity and increase in amorphousness of the plasticized electrolytes. To quantify the amorphousness or crystallinity of the samples, these diffractograms were also deconvoluted using the Origin 8.0 software.

Fig. 5.4: XRD pattern of (a) PVDF-HFP and (PVDF-HFP)-NaI-(EC/PC) electrolytes with various contents of (EC/PC) (in wt.%); (a) 10, (b) 20, (c) 30, (d) 40 and (e) 50

5.2.4 Deconvolution of X-ray Diffractograms for (PVDF-HFP)–NaI–EC/PC Electrolytes

The deconvolution of X-ray diffractograms was carried out in the range $2\theta = 5^\circ$ to 55° . The deconvoluted diffractograms for different (EC/PC) concentrations are presented in Fig. 5.5. From the deconvolution, the degree of crystallinity for all samples were calculated using equation 5.1. The results are listed in Table 5.3. From Table 5.3, it can be seen that degree of crystallinity for the polymer-salt complex added with 10 wt.% (EC/PC) was 24.4%. The amorphousness of the electrolyte has increased upon addition of plasticizer compared to the lowest degree of crystallinity at 34.9% obtained for the unplasticized sample with the composition 60 wt.% (PVDF-HFP) - 40 wt.% NaI shown in Fig. 5.3 (d). The d.o.c. dropped to 6.6% on addition of 20 wt.% (EC/PC). The value increased again on further addition of EC/PC to 9.0%, 11.0% and 20.0% with 30, 40 and 50 wt.% EC/PC addition respectively. The decrease in the degree of crystallinity indicates the increase in amorphousness of the samples. Sample with 20 wt.% (EC/PC) has the highest degree of amorphousness.

Fig. 5.5: Deconvoluted X-ray diffractograms of (PVDF-HFP)-NaI-(EC/PC) electrolytes having different (EC/PC) concentrations (in wt.%) (a) 10, (b) 20, (c) 30, (d) 40 and (e) 50

Table 5.3: Degree of crystallinity for (PVDF-HFP)-NaI-(EC/PC) polymer electrolytes having different (EC/PC) contents

5.3 XRD Studies for KI Containing Electrolytes

5.3.1 XRD for (PVDF-HFP) – KI system

Fig. 5.6 (a) to (g) show the X-ray diffractograms for pure (PVDF-HFP) and PVDF-HFP based polymer electrolytes with different KI concentrations ranging from 5 to 30 wt.% in steps of 5 wt.%. In Fig. 5.1 (a) the diffractogram for pure PVDF-HFP shows its crystalline characteristic peaks at $2\theta = 18.2^\circ$, 20.1° and 26.5° and 38.3° . It is clearly observed that upon the addition of KI, the crystalline peak at $2\theta = 26.5^\circ$ has disappeared in the diffractograms of all the polymer-salt complexes. The peak at $2\theta = 18.2^\circ$ has broadened for samples with 25 and 30 wt.% KI and has undergone changes in intensity for 5, 10, 15 and 20 wt.% KI. The elimination of crystalline peak is an indication of the reduction in crystallinity. In order to quantify the crystallinity of these electrolytes, the diffractograms were deconvoluted using Origin 8.0 software.

Fig. 5.6: XRD pattern for (a) Pure PVDF-HFP and (b) to (g) for (PVDF-HFP)-KI electrolytes having 5 to 30 wt.% KI in steps of 5 wt.%

5.3.2 Deconvolution of X-ray Diffractograms for (PVDF-HFP) – KI system

The deconvolution of X-ray diffractograms in the range $2\theta = 5^\circ$ to 55° were carried out. The deconvoluted diffractogram for different KI concentrations are presented in Fig. 5.7. Table 5.4 lists the degree of crystallinity (X_c) as function of salt concentration. As can be seen previously in Table 5.1, the d.o.c. for pure PVDF-HFP is 78.4%. Upon addition of 5 wt.% KI, d.o.c decreased to 57.1%. Further addition of KI concentration in the electrolyte decreased the d.o.c to the lowest value of 27.9% for the sample with 20 wt.% KI. The d.o.c value increases again on further addition as seen for 25 and 30 wt.% KI samples. The decrease in the d.o.c. indicates the increase in amorphousness of the samples and the sample having 20 wt.% KI is the most amorphous. This sample was then added with the EC/PC binary plasticizer to further improve the amorphousness of the electrolytes.

Fig. 5.7: Deconvoluted X-ray diffractograms for (PVDF-HFP)- KI electrolytes having (a) 5, (b) 10, (c) 15, (d) 20, (e) 25 and (f) 30 wt.% KI

Table 5.4: Degree of crystallinity for (PVDF-HFP)-KI polymer electrolytes having different KI concentrations

5.3.3 XRD for (PVDF-HFP) – KI – (EC/PC) Electrolytes

Fig. 5.8 displays X-ray diffractograms for plasticized (PVDF-HFP) – KI – EC/PC electrolyte system with EC/PC content varying from 10 to 60 wt.%. To quantify the amorphousness or crystallinity of the plasticized samples, the diffractogram of each sample was deconvoluted using the Origin 8.0 software.

Fig. 5.8: XRD pattern of (PVDF-HFP)-KI-(EC/PC) electrolytes having different wt.% of (EC/PC), (a)10, (b)20, (c)30, (d)40, (e)50 and (f)60

5.3.4 Deconvolution of X-ray Diffractograms for (PVDF-HFP-KI-(EC/PC) Electrolytes

Fig. 5.9 shows the XRD deconvolution for all plasticized polymer electrolytes. The deconvolution results are presented in Table 5.4. In Table 5.4, the d.o.c. for the sample with 10 wt.% (EC/PC) was calculated to be 26.5%. The amorphousness of the electrolyte has increased upon addition of plasticizer compared to the lowest degree of crystallinity, 27.9% obtained for the unplasticized (PVDF-HFP)-KI sample with composition 80 wt.% (PVDF-HFP) - 20 wt.% KI shown in Fig. 5.8 (d). The degree of crystallinity continued to drop on further addition of EC/PC until d.o.c reaches the lowest value of 13.6% for 50 wt.% (EC/PC). The decrease in d.o.c indicates the increase in the amorphousness of the sample. The sample having 50 wt.% (EC/PC) is the most amorphous.

Fig. 5.9: Deconvoluted X-ray diffractograms of (PVDF-HFP)-KI-(EC/PC) having different (EC/PC) concentrations (in wt.%); (a) 10, (b) 20, (c) 30, (d) 40, (e) 50 and (f) 60

Table 5.4: Degree of crystallinity for (PVDF-HFP)-KI-(EC/PC) polymer electrolytes having different (EC/PC) contents

5.4 Summary

X-ray diffraction have been carried out on pure (PVDF–HFP) film, polymer-salt electrolytes being (PVDF–HFP) – NaI and (PVDF–HFP) – KI and the corresponding plasticized electrolytes (PVDF–HFP) – NaI – (EC/PC) and (PVDF–HFP) – KI – (EC/PC). From X-ray diffraction studies, crystalline peaks for pure PVDF-HFP were observed at $2\theta = 18.2^\circ$, 20.1° , 26.5° and 38.3° . Upon addition of NaI and KI salts, crystalline peaks at $2\theta = 18.2^\circ$ and 20.1° have merged and shifted to $2\theta = 20.25^\circ$. The crystalline peak at $2\theta = 26.5^\circ$ disappeared in most samples. These changes show that complexation between polymer and salts has taken place and the semi-crystalline (PVDF–HFP) has become more amorphous with the addition of NaI and KI salts.

The increase in amorphousness has been quantified by the deconvolution technique using Origin 8.0 software. For (PVDF–HFP); the electrolytes with NaI has the lowest degree of crystallinity value of 34.9% for 40 wt.% NaI and the electrolytes with KI has the lowest degree of crystallinity of 27.9% for 20 wt.% KI. These results infer that these samples are the most amorphous. Upon addition of (EC/PC) plasticizer mixture, both samples have shown further reduction in the degree of crystallinity. For (PVDF–HFP) – NaI –(EC/PC) the lowest degree of crystallinity was 6.6% with 20 wt.% (EC/PC) and for (PVDF–HFP) – KI – (EC/PC) it was 13.6% with 50 wt.% (EC/PC) content. These results indicate that the use of plasticizers in (PVDF-HFP) based electrolytes have increased the amorphousness of the systems. The variation of d.o.c from XRD studies are consistent with the variation in amorphousness as deduced from FTIR investigations.