

CHAPTER 4

RESULTS ON FTIR STUDIES

4.1 Introduction

FTIR studies were carried out to investigate the interactions between various components and occurrence of complexation in the polymer electrolytes (Huang et al., 2013). FTIR can be used to analyse the interactions among ions in the systems. These interactions can induce changes in the vibrational modes of the molecules in the polymer electrolyte (Selvasekarapandian et al., 2005). The presence of free ions, ion pairs and ion aggregates can also be studied by FTIR spectroscopy technique (Kumar et al., 2005). Polymer electrolyte systems characterized by Fourier transform infrared (FTIR) spectroscopy in this work are:

- (i) x wt. % (PVDF-HFP) – y wt. % NaI, where $x = 100, 90, 80, 70, 60, 50$ and $y = 0, 10, 20, 30, 40$ and 50 .
- (ii) x wt. % [(PVDF-HFP)/NaI] – y wt. % (EC/PC), where $x = 90, 80, 70, 60, 50$ and $y = 10, 20, 30, 40$ and 50 ; (PVDF-HFP)/NaI fixed at 60/40 wt. ratio.
- (iii) x wt. % (PVDF-HFP) – y wt. % KI, where $x = 95, 90, 85, 80, 75, 70$ and $y = 5, 10, 15, 20, 25$ and 30 .
- (iv) x wt. % [(PVDF-HFP)/KI] – y wt. % (EC/PC), where $x = 90, 80, 70, 60, 50$ and $y = 10, 20, 30, 40, 50$ and 60 ; (PVDF-HFP)/KI fixed at 80/20 wt. ratio.

FTIR was used to confirm the interactions between PVDF-HFP, NaI and EC/PC in the first electrolyte system and between PVDF-HFP, KI, and EC/PC in the latter. When interactions occur in the polymer system, changes in the vibrational modes of the

molecules in the material could be observed from the changes or shifting in the wavenumbers.

4.2 The Infrared Spectrum of PVDF-HFP

In these studies, poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) is used as the polymer host in the electrolytes. PVDF-HFP copolymers have fluorinated monomers $[-CF_2-CF-CF_3-]$ randomly added to the $[-CH_2-CF_2-]$ main chain of PVDF homopolymer. The $[-CF_3-]$ molecular bonds are branched to the main chain (Liz et al., 2011). FTIR is used to confirm the interactions of PVDF-HFP with salts and plasticizer. There are many reports in the literature on the infrared spectrum of PVDF-HFP in polymer electrolytes by many researchers including Song et al., (2003), Li et al., (2005), Saikia et al., (2011), Ramesh and Lu (2011), Aravindan et al., (2008) and Sim et al., (2012).

Fig. 4.1 shows the infrared spectrum of PVDF-HFP film obtained using the FTIR-Spectrophotometer (Thermo Scientific/ Nicolet iS10) in the region between 700 to 2000 cm^{-1} and 2000 – 4000 cm^{-1} . The prominent bands observed are indicated in the figure. Table 4.1 lists the vibrational modes of PVDF-HFP that have been reported by the above mentioned researchers. The PVDF-HFP film was prepared by dissolving the polymer pellet in acetone at 60 °C and casting at room temperature to allow solvent evaporation and film formation. It can be observed that most of the bands in Table 1 appear in the infrared spectrum of PVDF-HFP in Fig. 4.1.

Fig. 4.1: FTIR spectrum for pure PVDF-HFP film in the range (a) 650 to 2000 cm^{-1} and (b) 2000 to 4000 cm^{-1}

Table 4.1: The characteristic vibrational modes and wavenumbers of PVDF-HFP

Vibrational mode	Wavenumbers (cm ⁻¹)	References
Crystal phase of (PVDF-HFP)	760, 853, 976, 1072	Li et al., (2005), Ramesh and Lu (2011)
Amorhous phase of (PVDF-HFP)	841, 871, 879	Li et al., (2005), Aravindan et al., (2008), Ramesh and Lu (2011),
CH ₂ rocking	851	Ramesh and Lu (2011)
out of plane C–H bending	972	Ramesh and Lu (2011)
C–C skeleton vibration	1062	Ramesh and Lu (2011)
Symmetrical stretching mode of CF ₃	1069	Aravindan et al., (2008)
CF ₂ stretching	1147	Ramesh and Lu (2011)
Symmetrical stretching mode of CF ₃	1179	
Symmetrical stretching mode of CF ₂	1185	Aravindan et al., (2008)
Assymmetric stretching vibrations of CF ₂	1197	Aravindan et al., (2008)
Symmetrical stretching vibrations of CF ₂	1276	Aravindan et al., (2008)
CF stretching	1382, 1400	Ramesh and Lu (2011),
Symmetrical vibration of CH ₂ groups	2980	Li et al., (2005)
Nonsymmetrical vibration of CH ₂ groups	3022	Li et al., (2005)

4.3 Infrared Spectrum of EC, PC and the EC/PC Mixture

A mixture containing equal weight ratio of ethylene carbonate (EC) and propylene carbonate (PC) have been used as plasticizer in this work. Figure 4.2 shows the structure of EC and PC. Tables 4.2 and 4.3 list the characteristic FTIR bands for EC and PC reported by some previous researchers. The infrared spectra of EC, PC and the mixture of EC/PC used in the preparation of electrolytes in this work are shown in Fig. 4.3(a) and (b). It can be observed that most of the bands for pristine EC and PC in the infrared

spectra in Fig. 4.3 (a) and (b) are close to the finding of Ikezawa and Nishi (2007), Song et al., (2003), Starkey and Frech (1996), Deepa et al., (2004), Ali et al., (2008) and Kanamura (2001).

Fig. 4.2: The chemical structure of (a) EC and (b) PC

Table 4.2: The characteristic vibrational modes and wavenumbers of EC

Vibrational mode (EC)	Wavenumbers (cm ⁻¹)	References
C = O bending	717	Chintapalli and French, 1996
Scissoring of CH ₂	1154	Song et al., 2003
CH ₂ wagging	1390, 1420	Song et al., 2003; Wang et al., 1996
CH ₂ bending	1479	Song et al., 2003
C = O stretching	1770, 1796, 1810, 1870 1772, 1799	Ikezawa and Nishi, 2005 Song et al., 2003
Ring breathing	890, 1067	Wang et al., 1996
CH ₃ asymmetric stretching	3036	Ramesh et al., 2011

The FTIR spectra of EC and PC are shown in Fig. 4.3 (a) (i) – (ii) and Fig. 4.3 (b) (i) – (ii). For the mixture with equal weights EC and PC, the FTIR spectra in Fig. 4.3 (a) (iii) and Fig. 4.3 (b) (iii) display combination peaks from both pristine EC and PC

characteristic peaks. Some of the peaks are mentioned here to show that interactions have occurred between EC and PC. C=O stretching peaks for pristine EC which were originally at 1766 and 1792 cm^{-1} were observed in the EC/PC mixture band, but slightly shifted to 1769 and 1882 cm^{-1} respectively. PC peaks corresponding to symmetric ring deformation at 708 cm^{-1} disappeared in the EC/PC mixture solution. PC peaks at 940, 950, 1545, 1444, 1386 cm^{-1} did not show much shifting and were observed at locations 941, 951, 1546, 1442 and 1387 cm^{-1} respectively in the EC/PC mixture band. These findings indicate that both EC and PC have mixed well and can be used as a binary plasticizer solution.

Table 4.3: The characteristics vibrational modes and wavenumbers of PC

Vibrational mode	Wavenumbers (cm^{-1})	References
Ring stretching breathing mode	841	Ali et al., 2008; Kanamura, 2011
C - O stretching	940	Ali et al., 2008; Kanamura, 2011
Ring stretching + Ring breathing	957, 950, 920, 850	Deepa et al., 2004
Symmetrical CH bending	1350	Ali et al., 2008; Kanamura, 2011
CH wagging	1386	Ali et al., 2008; Kanamura, 2011
2 \times symmetric ring deformation	1410, 712	Deepa et al., 2004
CH ₂ bending of CH ₃	1450	Deepa et al., 2004
CH ₂ scissoring	1485	Deepa et al., 2004
CH ₂ rocking + Ring breathing	1557	Deepa et al., 2004
C = O symmetric stretching	1737, 1732, 1730, 1720	Deepa et al., 2004
C = O stretching	1777	Starkey and Frech, 1996
2 \times ring breathing mode	1900, 950	Deepa et al., 2004

Fig. 4.3 (a): FTIR spectrum of (i) EC, (ii) PC and (iii) the mixture of EC/PC at 1/1 wt. ratio in from 700 to 2000 cm^{-1}

Fig. 4.3 (b): FTIR spectrum of (i) EC, (ii) PC and (iii) the mixture of EC/PC at 1/1 wt. ratio in from 2000 to 4000 cm^{-1}

4.4 Infrared Spectrum of NaI and KI

Fig. 4.4 (a) displays the infrared spectra of sodium iodide (NaI) and potassium iodide from 650 cm^{-1} to 2000 cm^{-1} and Fig. 4.4 (b) displays the infrared spectra of sodium iodide (NaI) and potassium iodide from 2000 cm^{-1} to 4000 cm^{-1} that have been used as dopant salts for polymer electrolytes in these studies. It can be seen that peaks for NaI occur at $1348, 1380, 1604, 1619, 3205, 3415$ and 3463 cm^{-1} while for KI occur at $1341, 1375, 1578$ (very small) and 3449 cm^{-1} . The very small peaks are not even mentioned in some references e.g. in Thompson (1996). 1604 and 1619 cm^{-1} peaks in NaI might be due to water adsorbance which are close to the finding of Thompson (1996). In his Infra-Red Spectroscopic Studies of Aqueous Systems, he has mentioned that water H-O-H scissoring mode near 1640 cm^{-1} shows an observable decrease in wave number to around 1610 cm^{-1} with iodide solutions. In Fig. 4.4 (b), peaks at $3205, 3415, 3449$ and 3463 cm^{-1} are water absorbance peaks where 3415 cm^{-1} is water H-O-H stretching wave number, 3449 and 3463 cm^{-1} are OH stretching.

Fig. 4.4 (a): FTIR spectrum of (i) KI and (ii) NaI in the range from 650 to 2000 cm^{-1}

Fig. 4.4 (b): FTIR spectrum of (i) KI and (ii) NaI in the range from 2000 to 4000 cm^{-1}

4.5 Intermolecular Interaction between PVDF-HFP and NaI

Addition of NaI into the polymer host results in interactions or complexation between the salt and the host polymer matrix. This interaction can influence local structure of the polymer back-bones and significantly affects ionic mobility (Prajapati and Gupta, 2011). FTIR spectra for the polymer-salt system at compositions x wt.% (PVDF-HFP) – y wt.% NaI, where $x = 90, 80, 70, 60, 50$ and $y = 10, 20, 30, 40$ and 50 have been taken and compared to the pure polymer spectrum in Fig. 4.1 and the infrared spectrum of sodium iodide salt (NaI) in Fig. 4.4 to investigate the interactions between polymer and salt. The infrared spectra in the wavenumber range from 650 to 1000 cm^{-1} are displayed in Fig. 4.5. From Fig. 4.1, characteristic peaks for pure PVDF-HFP are observed at 761, 795, 839, 851, 871, 972, 1062, 1145, 1179, 1197, 1276, 1381, 1397, 1401, 1416, 1440, 1781, 1787, 2985 and 3022 cm^{-1} .

After addition of NaI, PVDF-HFP crystalline peaks at 761, 795 and 972 and 1381 cm^{-1} are disappeared. The peak at 851 cm^{-1} which is assigned to CH_2 rocking vibration in PVDF-HFP has reduced in intensity and almost disappeared. In Fig. 4.5 (iii) to (viii), amorphous peak at 871 cm^{-1} in the pure PVDF-HFP has shifted to 877, 876, 877, 877 and 877 cm^{-1} respectively.

Fig. 4.6 shows the infrared spectra in the range 1000 to 1500 cm^{-1} . From this figure it can be seen that the C-C skeleton band at 1062 cm^{-1} has become less broad in the polymer – salt spectrum and had shifted to 1069, 1070, 1070, 1069 and 1069 cm^{-1} respectively for different NaI contents. CF_2 stretching peak at 1145 cm^{-1} has become broader and shifted to a lower wavenumber at 1131 cm^{-1} . The 1179 cm^{-1} peak, which is a CF_3 symmetrical stretching has also broadened and shifted to a lower wavenumber at 1166 cm^{-1} . Asymmetric stretching vibrations of CF_2 band at 1197 cm^{-1} has become less broad and far shifted to a higher wavenumber of 1228 cm^{-1} . CF_2 stretching at 1381 merged with another CF_2 stretching mode at 1401 cm^{-1} and peaked at 1398 cm^{-1} .

From changes in PVDF-HFP band that include shifting of PVDF-HFP characteristic peaks, formation of new peaks and disappearance of peaks after the addition of NaI, it can be concluded that the polymer and salt have interacted.

Fig. 4.5: FTIR spectra of (i) NaI, (ii) pure PVDF-HFP and (iii) to (vii) FTIR spectra for (PVDF-HFP) with 10 to 50 wt.% NaI in the range 700 to 1000 cm^{-1}

Fig. 4.6: FTIR spectra of (i) NaI, (ii) pure PVDF-HFP and (iii) to (vii) FTIR spectra for (PVDF-HFP) with 10 to 50 wt.% NaI in the range 1000 to 1500 cm^{-1}

Fig. 4.7 below shows the schematic of the (PVDF-HFP)-MI, ($M = Na, K$) interaction. Fluorine is the electron-donating atom in PVDF-HFP. The cation of the salt will form a dative bond with fluorine to form (PVDF-HFP) – salt complexes.

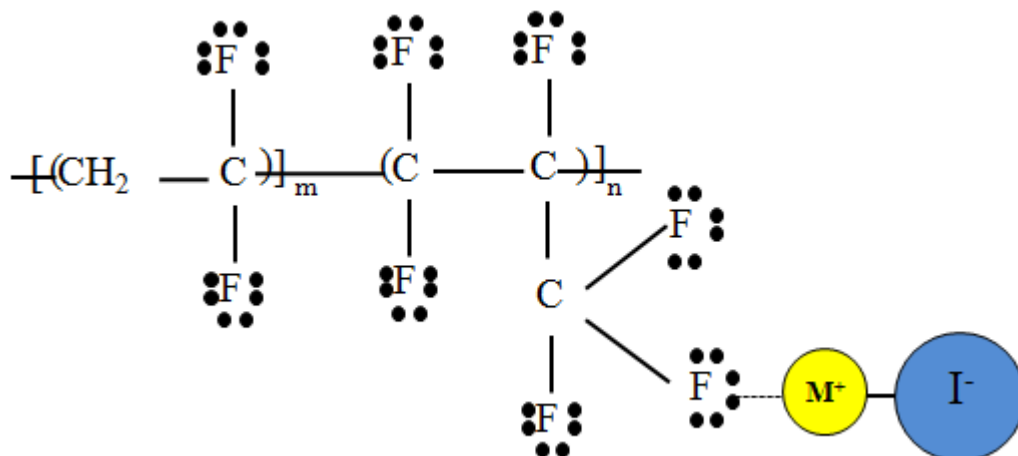


Fig. 4.7: Schematic diagram of (PVDF-HFP) – MI interaction ($M = Na, K$)

Due to the disappearance of crystalline peaks and the shifting of amorphous peaks it is believed that the addition of NaI has reduced the crystallinity and hence increased amorphousness in the electrolytes. Using Origin 8.0 software, areas under the shifted amorphous peaks at 871 cm^{-1} for all salt concentrations have been calculated to see the effect of salt content on the degree of crystallinity.

Fig. 4.8 (a) to (e) show the shifted amorphous peak of PVDF-HFP (870 cm^{-1}) for polymer electrolytes containing 10 to 50 wt.% NaI respectively. The area under each peak (calculated by Origin 8.0 software) for the respective samples are listed in Table 4.4 and presented graphically in Fig. 4.9.

It can be inferred that the addition of NaI has increased the amorphous domain. However, the amorphous phase may have reached saturation at 40 wt.% NaI. Further increase in

NaI content did not increase the amorphous phase and could possibly induce same crystalline peak due to recrystallization of the salt at 50 wt.% NaI.

Fig. 4.8: Area under amorphous peak calculated with Origin 8.0 software at different NaI concentrations (in wt.%); (a) 10, (b) 20, (c) 30, (d) 40 and (e) 50.

Table 4.4: Area under amorphous peak calculated with Origin 8.0 software for different NaI content

NaI (wt.%)	Area under amorphous peak (a.u.)
10	4.23
20	4.62
30	4.86
40	5.26
50	5.23

Fig. 4.9: Area under amorphous peak calculated with Origin 8.0 software for different NaI concentrations (in wt.%); (a) 50, (b) 20, (c) 30, (d) 40 and (e) 50.

4.6 Intermolecular Interaction between PVDF-HFP, NaI and EC/PC

The formation of complexes between polymer and salt in the (PVDF-HFP) - NaI electrolytes has been proven in the previous section. Plasticized electrolytes have been prepared by incorporating a plasticizer system into the (PVDF-HFP)-NaI complexes with compositions of x wt. % [(PVDF-HFP)-NaI] – y wt. % (EC/PC), where $x = 90, 80, 70, 60, 50$ and $y = 10, 20, 30, 40$ and 50 while keeping (PVDF-HFP)-NaI fixed at 60:40 wt. ratio since this composition exhibits the highest amorphous phase. The plasticizer was a 1:1 weight ratio EC/PC mixture.

FTIR was used to study the interaction between polymer, salt and the plasticizer. Fig. 4.10 (a) displays the infrared spectra of plasticized polymer electrolytes, with various plasticizer contents, in the wavenumber ranging from 650 to 1000 cm^{-1} and Fig. 4.10 (b) displays the FTIR spectra from 1000 to 4000 cm^{-1} . These spectra were analyzed by comparing with infrared characteristic bands of PVDF-HFP, NaI and EC/PC discussed previously. From Fig. 4.10 (a) (ii) to (vi), it is clearly seen that the infrared spectra of the plasticized electrolytes contain PVDF-HFP and (EC/PC) characteristic peaks. EC band of C = O bending at 714 cm^{-1} was reduced in intensity and slightly shifted to 718 cm^{-1} for all EC/PC contents in the (PVDF-HFP)-NaI-EC/PC spectra. After addition of (EC/PC), PVDF-HFP crystalline peaks at 761, 795 and 972 and 1381 cm^{-1} have disappeared. Amorphous peak at 871 cm^{-1} in the pure PVDF-HFP has shifted to 877, 876, 877, 877 and 878 cm^{-1} respectively with NaI content of 10, 20, 30, 40, and 50 wt.% NaI.

In order to prove that interaction between PVDF-HFP, NaI and EC/PC mixture has taken place in the plasticized electrolytes, FTIR spectra of salt - plasticizer and polymer-plasticizer were studied. The infrared spectrum of the NaI – (EC/PC) mixture and the

spectrum of the mixture of PVDF-HFP and EC/PC were also recorded. Figure 4.11 shows the FTIR spectrum of NaI-(EC/PC) mixture and Fig. 4.12 shows the spectrum of (PVDF-HFP)-(EC/PC). Both spectra were compared with the spectrum of the (EC/PC) mixture.

Fig. 4.10(a): FTIR spectra of (i) pure PVDF-HFP, (ii) to (vi) plasticized (PVDF-HFP) - NaI electrolytes with 10 to 50 wt.% (EC/PC) and (vii) (EC/PC) mixture at 1/1 wt. ratio in the range 650 to 1000 cm^{-1}

Fig. 4.10 (b) : FTIR spectra of (i) pure PVDF-HFP, (ii) to (vi) plasticized (PVDF-HFP)-NaI electrolytes with 10 to 50 wt.% (EC/PC) and (vii) (EC/PC) mixture at 1/1 wt. ratio in the range 1000 to 2000 cm^{-1}

Fig. 4.11 (i) shows the infrared spectrum of the mixture of NaI-(EC/PC). The EC and PC bands (770, 1044, 1546, 1769, 1782 cm^{-1}) are clearly seen in the spectrum. Ring breathing for EC at 891 cm^{-1} has been shifted to 899 cm^{-1} . CH_2 scissoring band (1156 cm^{-1}) has shifted to a higher wavenumber of 1178 cm^{-1} . The changes in the EC/PC

infrared spectrum upon addition of NaI indicate that there are interactions between salt and plasticizer in the plasticized electrolytes.

Fig. 4.11: FTIR spectra of (i) NaI-(EC/PC) mixture and (ii) (EC/PC) mixture at 1/1 wt. ratio in the range 650 to 2000 cm^{-1}

Fig. 4.12 (i) and (iii) show the individual infrared spectrum of pure PVDF-HFP and (EC/PC) plasticizer and their characteristic bands before mixing. Fig. 4.12 (ii) shows the infrared spectrum of the mixture of (PVDF-HFP)-(EC/PC). In Fig. 4.12 (ii), the EC and PC bands are clearly seen in the spectrum. After addition of EC/PC, the PVDF-HFP crystalline peaks at 761 , 795 and 972 and 1381 cm^{-1} disappeared. EC/PC peaks are seen in the polymer-plasticizer mixture. The changes in the PVDF-HFP peaks and the formation of EC/PC peaks such as 714 , 770 , 1044 , 1066 , 1115 , 1351 , 1769 and 1762 cm^{-1} in the (PVDF-HFP) - EC/PC mixture indicate that there are interactions between the polymer and plasticizer in the plasticized electrolytes.

Fig. 4.12: FTIR spectra of (i) pure (PVDF-HFP), (ii) (PVDF-HFP) - (EC/PC) mixture and (iii) (EC/PC) mixture at 1/1 wt. ratio in the range 650 to 2000 cm^{-1}

Due to the disappearance of crystalline peaks and the shifting and broadening of the amorphous peaks, it is believed that the addition of EC/PC has reduced the crystallinity and hence increases amorphousness in the electrolytes. Using Origin 8.0 software, area under each shifted amorphous peak at 871 cm^{-1} (Fig. 4.10 (a)) for all EC/PC contents has been calculated to see the effect of plasticizer content on the degree of crystallinity. The calculated area from Origin 8.0 software are shown in Fig. 4.13. The results are summarized in Table 4.5 and represented graphically in Fig. 4.14. It can be

inferred that the addition of EC/PC has increased the amorphous domain which reaches a maximum value at 20 wt.% EC/PC.

Fig. 4.13: Area unde amorphous peak calculated with Origin 8.0 software for different (EC/PC) concentrations (in wt.%); (a) 10, (b) 20, (c) 30, (d) 40 and (e) 50

EC/PC (wt.%)	Area under amorphous peak (a.u.)
10	5.27
20	5.30
30	5.28
40	5.26
50	5.23

Table 4.5: Area under amorphous peak calculated with Origin 8.0 software for different (EC/PC) content

Fig. 4.14: Area under amorphous peak calculated with Origin 8.0 software for (EC/PC) concentrations (in wt.%); (a)50, (b)20, (c)30, (d)40 and (e) 50.

4.7 Intermolecular Interaction between PVDF-HFP and KI

FTIR is used to study the (PVDF-HFP) – KI complexes formation. KI was added to PVDF-HFP to have the compositions of x wt.% (PVDF-HFP) – y wt.% KI, where $x = 95, 90, 85, 80, 75, 70$ and $y = 5, 10, 15, 20, 25$.

Infrared spectra of PVDF-HFP electrolytes with different KI contents are shown in Fig. 4.15. (from 700 cm^{-1} to 1000 cm^{-1}) and Fig. 4.16 (from 1000 cm^{-1} to 1600 cm^{-1}). Infrared spectrum of PVDF-HFP is also given to show the characteristic bands of PVDF-HFP before the formation of the polymer-salt complexes. Same as in the NaI electrolyte system, it can be seen from Fig. 4.15, the PVDF-HFP crystalline peaks at $761, 795$ and 972 cm^{-1} disappeared after the addition of addition of KI. The PVDF-HFP peak at 851 cm^{-1} which is assigned to CH_2 rocking vibration in PVDF-HFP has reduced in intensity and disappeared for large salt contents. The amorphous peaks at 871 cm^{-1} had shifted to $877, 876, 876, 877, 877$ and 877 cm^{-1} respectively as the salt content was increased.

From Fig. 4.16, it can be seen that the PVDF-HFP CF_2 stretching at 1381 cm^{-1} merged with another CF_2 stretching mode at 1401 cm^{-1} and peaked at 1397 cm^{-1} after the addition of KI. C-C skeleton band at 1062 cm^{-1} has become less broad and sharp in the polymer – salt spectrum and has shifted to $1067, 1067, 1067, 1069, 1069$ and 1069 cm^{-1} respectively for different KI contents. CF_2 stretching peak at 1145 cm^{-1} has merged with another band at 1179 cm^{-1} , appeared broader with lower intensity, and peaked at 1167 cm^{-1} . The 1197 cm^{-1} peak, which is a CF_3 symmetrical stretching has also broadened and shifted to higher wavenumber at 1227 cm^{-1} .

Fig. 4.15: FTIR spectra of (i) pure (PVDF-HFP) and (ii) to (vii) (PVDF-HFP)-KI with 5 to 30 wt.% KI in the range 700 to 1000 cm^{-1}

Fig. 4.16: FTIR spectra of (i) pure PVDF-HFP and (ii) to (vii) (PVDF-HFP)-KI with 5 to 30 wt.% KI in the range 1000 to 2000 cm^{-1}

Due to the disappearance of crystalline peaks and the shifting and broadening of the amorphous peaks, it is believed that the addition of KI has reduced the crystallinity in the electrolytes. Using Origin 8.0 software, area under each amorphous peak (871 cm^{-1}) shown in Fig. 4.15 has been calculated to see the effect of salt content on the degree of crystallinity. The calculated area from Origin 8.0 software are shown in Fig. 4.17. The results are summarized in Table 4.6 and represented graphically in Fig. 4.18. From the calculated area for all salt concentrations, it can be inferred that the addition of KI has

increased the amorphous domain which reaches a maximum value at 20 wt.% KI and decreases thereafter for higher salt concentrations.

Fig. 4.17: Area under amorphous peak calculated with Origin 8.0 software for different KI concentrations (in wt.%); (a) 5, (b) 10, (c) 15, (d) 20, (e) 25 and (e) 30.

Table 4.6: Area under amorphous peak calculated with Origin 8.0 software for different KI contents

KI (wt.%)	Area under amorphous peak (a.u.)
5	4.13
10	4.22
15	4.26
20	4.35
25	4.31
30	4.30

Fig. 4.18: Area under amorphous peak calculated with Origin 8.0 software for different KI concentrations (in wt.%); (a) 5, (b) 10, (c) 15, (d) 20, (e) 25 and (e) 30

4.8 Intermolecular Interaction between PVDF-HFP, KI and (EC/PC)

Plasticized electrolyte has been prepared by incorporating plasticizer into the (PVDF-HFP)-KI complexes to have the compositions of x wt. % [(PVDF-HFP)/KI] – y wt. % (EC/PC), where $x = 90, 80, 70, 60, 50$ and $y = 10, 20, 30, 40, 50$ and 60 while keeping the (PVDF-HFP)/KI fixed at 80/20 weight ratio. The plasticizer was a 1:1 weight ratio EC/PC mixture.

To see the interaction between polymer, salt and plasticizer in KI systems, the infrared spectra of the plasticized and unplasticized electrolytes were compared. These two spectra are displayed together with the spectra of PVDF-HFP and EC/PC mixture in Fig. 4.19 (in the wavenumber range 700 to 1000 cm^{-1}) and 4.20 (in the range 1000 to 2000 cm^{-1}). The unplasticized electrolyte has the composition of x wt. % (PVDF-HFP) – y wt. % (KI), where $x = 80$ and $y = 20$ and the plasticized electrolyte has the composition of x wt. % [(PVDF-HFP)/KI] – y wt. % (EC/PC), where $x = 50$ and $y = 50$: (PVDF-HFP)/KI fixed at 80/20 wt. ratio.

It is clearly seen from Fig. 4.19 (ii) and (iii) and Fig. 4.20 (ii) and (iii) that the addition of KI has eliminated the PVDF-HFP crystalline peaks at 761, 795 and 972 and 1381 cm^{-1} and shifted amorphous peaks at 871 cm^{-1} to higher wavenumbers. Upon addition of plasticizer, new peaks at 714, 970, 1066, 1769 and 1782 cm^{-1} due to C-O bending in EC, EC skeletal stretching, EC ring breathing, C=O stretching in PC and C=O symmetric stretching in PC respectively have occurred in the plasticized electrolyte indicating that the plasticizer has mixed well with the salt and polymer.

Fig. 4.19: FTIR spectra of (i) pure PVDF-HFP (ii) (PVDF-HFP)-KI complexes (iii) (PVDF-HFP)-KI-(EC/PC) and (iv) (EC/PC) in the range 700 to 1000 cm^{-1}

Fig. 4.20: FTIR spectra of (i) pure PVDF-HFP (ii) (PVDF-HFP)-KI complexes (iii) (PVDF-HFP)-KI-(EC/PC) and (iv) (EC/PC) in the range 1000 to 2000 cm^{-1}

Fig. 4.21 displays the infrared spectra for (PVDF-HFP)-KI-(EC/PC) electrolytes, showing the shifting of the amorphous peak (originally at 871 cm^{-1} in pure PVDF-HFP infrared spectra) for all EC/PC concentrations. After addition of (EC/PC), the amorphous peak at 871 cm^{-1} has shifted to 877 cm^{-1} in all samples. Using Origin 8.0 software, area under each amorphous peak has been calculated to see the effect of plasticizer content on the degree of crystallinity in the (PVDF-HFP)-KI-(EC/PC

electrolytes. The calculated area from Origin 8.0 software are shown in Fig. 4.22. The results are summarized in Table 4.7 and represented graphically in Fig. 4.23. The results inferred that the addition of plasticizer has increased the amorphous domain which reaches a maximum value at 50 wt.% EC/PC concentration.

Fig. 4.21: FTIR spectra for (i) pure (PVDF-HFP) and (ii) to (vii) (PVDF-HFP) -KI-(EC/PC) at different EC/PC concentration (in wt.%); (a) 10, (b) 20, (c) 30, (d) 40, (e) 50 and (f) 60.

Fig. 4.22: Area under amorphous peak calculated with Origin 8.0 software at different (EC/PC) concentrations (in wt.%); (a) 10, (b) 20, (c) 30, (d) 40, (e) 50 and (f) 60.

Table 4.7: Area under amorphous peak calculated with Origin 8.0 software at different EC/PC content

(EC/PC) (wt. %)	Area under amorphous peak (a.u.)
10	4.33
20	4.35
30	4.37
40	4.42
50	4.45
60	4.44

Fig. 4.23: Area under amorphous peak calculated with Origin 8.0 software at different (EC/PC) concentrations (in wt.%); (a) 10, (b) 20, (c) 30, (d) 40, (e) 50 and (f) 60.

4.9 Summary

FTIR studies have shown that PVDF-HFP polymer forms polymer-salt complexes with both NaI and KI salts and there are also interactions between polymer and plasticizer and between salt and plasticizer. The elimination of crystalline peaks after the addition of salt and plasticizer indicate the enhancement in the amorphousness of the electrolytes which is good for ionic conduction. The area of the band representing the amorphous region varies with salt and plasticizer concentration.