

CHAPTER 5

X-RAY DIFFRACTION ANALYSIS

5.1 INTRODUCTION

From the previous chapter, it is known that by the solution cast technique, polymer electrolytes have been prepared. In this chapter, results on x-ray diffraction studies of chitosan-NH₄I electrolytes, (chitosan-PVA)-NH₄I electrolytes, (chitosan-PEO)-NH₄I electrolytes and chitosan-NH₄I-IL electrolytes will be presented. The objective of this chapter is to understand the nature of the different electrolyte systems. The formation of complexes can also be known from the shift in diffraction peaks from the original position and/or if new crystalline peaks are observed in the XRD pattern (Sekhon *et al.*, 1995). The absence of peaks due to the increase in amorphousness of the sample can also indicate the occurrence of complexation.

5.2 CHITOSAN-NH₄I SYSTEMS

The X-ray diffraction patterns of pure chitosan film and the chitosan-NH₄I electrolytes are shown in Figure 5.1. The crystalline peaks of pure chitosan film are observed at $2\theta = 11.5^\circ$ and 22.7° . It can be clearly seen that the crystalline peak at $2\theta = 11.5^\circ$ has disappeared upon addition of NH₄I. The absence of peaks for electrolytes designated Ch2 to Ch10 in Figure 5.1 indicates that the chitosan-NH₄I electrolytes are more amorphous than the chitosan membrane. To know the change in nature upon addition of NH₄I, the full width at half maximum (FWHM) of the amorphous halo has been calculated using the Origin 8 software.

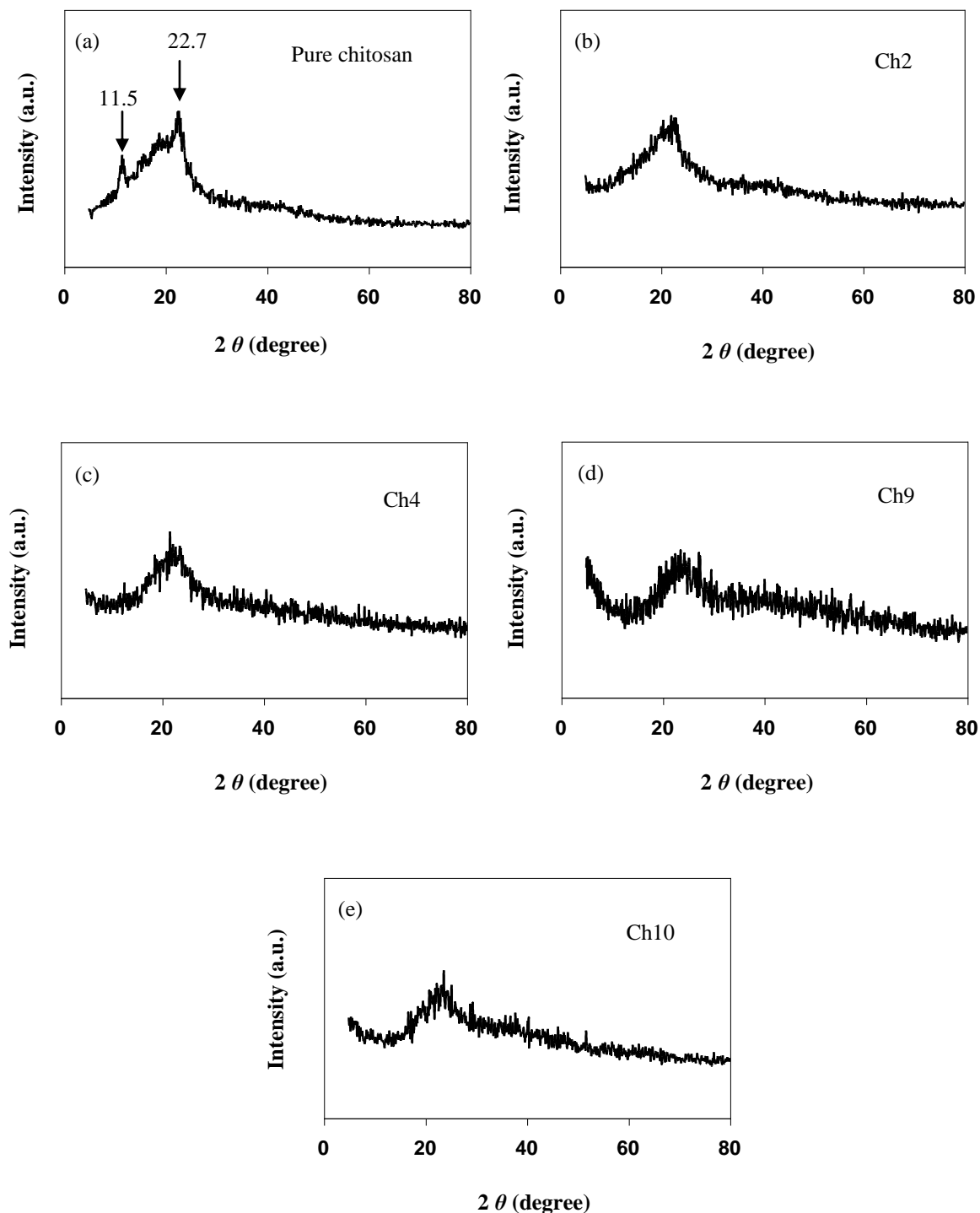
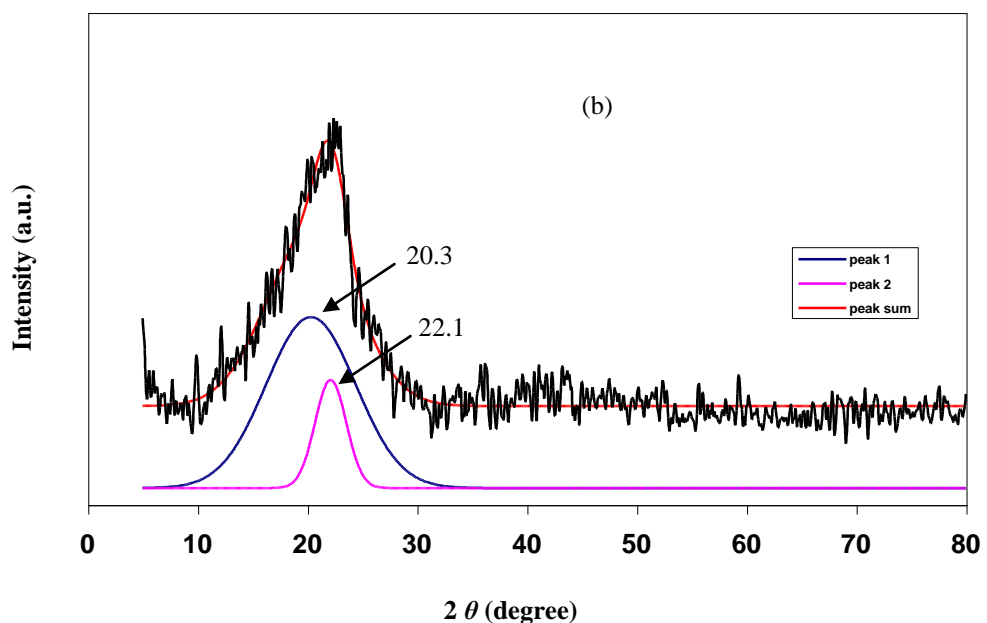
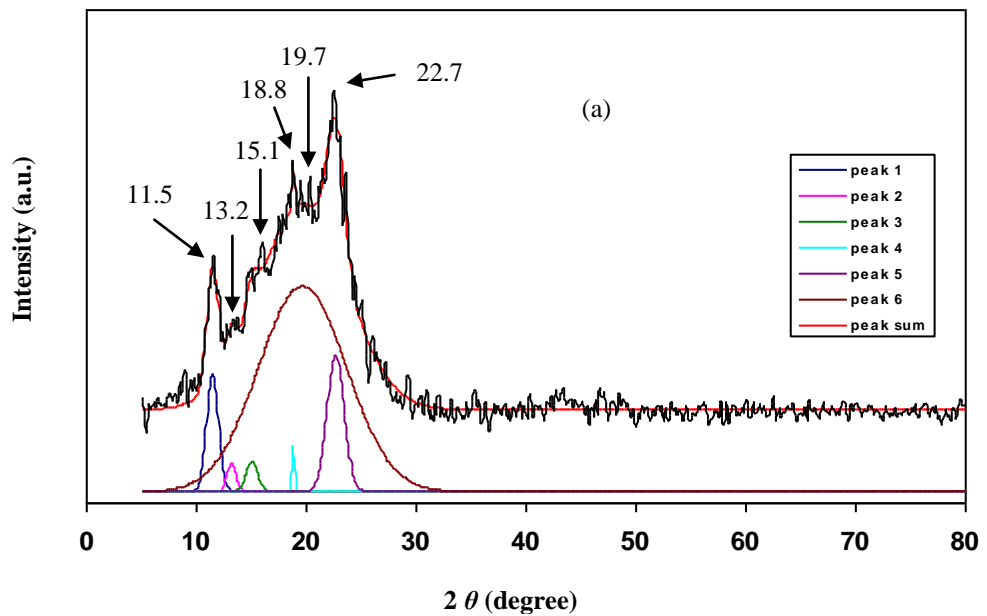


Figure 5.1: X-ray diffraction patterns for (a) pure chitosan film and electrolytes containing (b) 90 wt.% chitosan-10wt.% NH_4I (c) 80 wt.% chitosan-20wt.% NH_4I (d) 55 wt.% chitosan-45wt.% NH_4I and (e) 50 wt.% chitosan-50wt.% NH_4I

Figure 5.2 depicts the results of gaussian fitting on selected films using the Origin 8 software. It can be observed that the diffractogram of the pure chitosan film (Ch0) have additional crystalline peaks at $2\theta = 13.2^\circ$, 15.1° , 18.8° and 19.7° apart from readily obvious peaks at $2\theta = 11.5^\circ$ and 22.7° in Figure 5.1 (a). Deconvolution of the diffractogram for sample Ch2 indicates that the single halo in Figure 5.1 (b) consists of two peaks at $2\theta = 20.3^\circ$ and 22.1° .



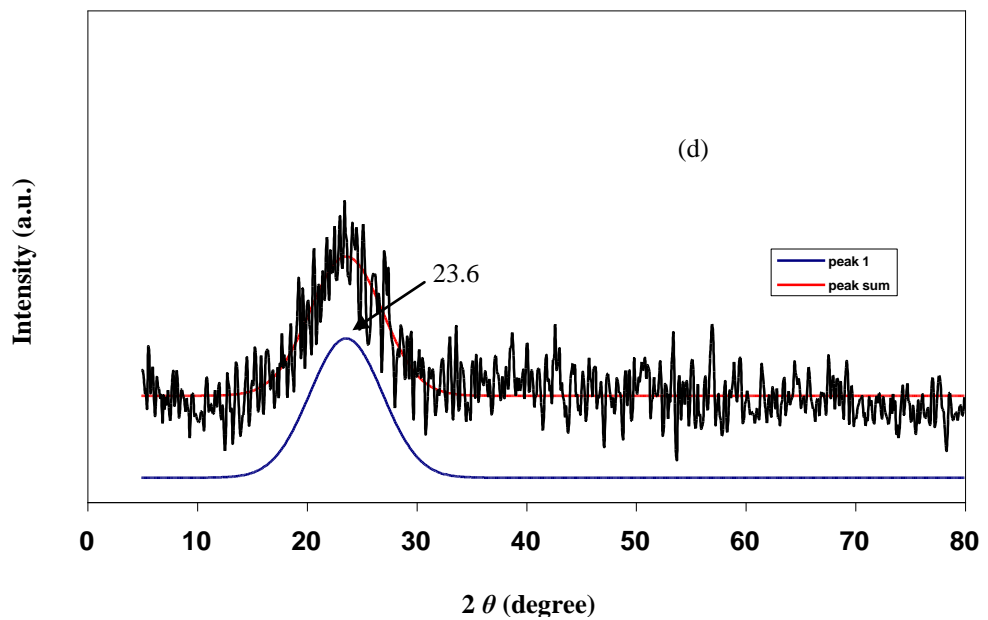
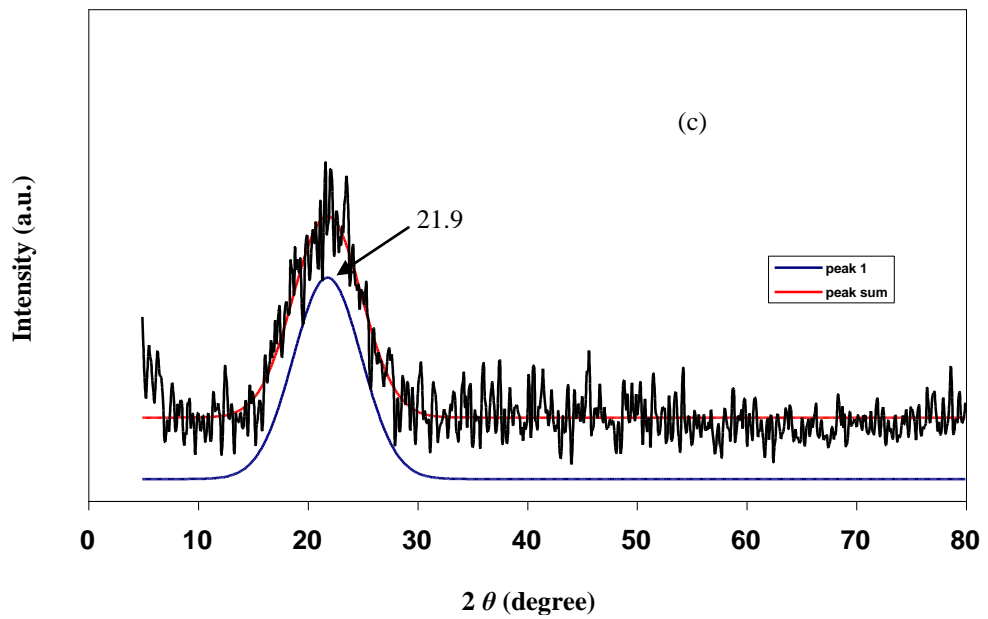


Figure 5.2: Gaussian fitting of XRD for (a) pure chitosan film and electrolytes containing (b) 90 wt.% chitosan-10wt.% NH_4I (Ch2) (c) 80 wt.% chitosan-20wt.% NH_4I (Ch4) and (d) 55 wt.% chitosan-45wt.% NH_4I (Ch9)

At this juncture, samples Ch4 and Ch9 can be inferred to be more amorphous than sample Ch2. In order to determine which of the two samples Ch4 or Ch9 is the more amorphous, the full width at half maximum height of the peaks is obtained from Origin 8 software. With this, the crystallite size, D and degree of crystallinity, χ (%) are calculated using equation 5.1 and 5.2 respectively. Table 5.1 shows the FWHM, crystallite size, D and degree of crystallinity for selected chitosan-NH₄I electrolytes.

$$D = \frac{0.9 \lambda}{FWHM \cos \theta} \quad (5.1)$$

$$\chi (\%) = \frac{S}{S_0} \times 100 \quad (5.2)$$

Where S is sum area of all crystalline peaks and S_0 is the sum area of crystalline peaks and amorphous hump. λ is the X-ray wavelength (1.5406 Å).

Table 5.1: FWHM, D and χ (%) for selected chitosan-NH₄I electrolytes

Electrolytes	2θ (degree)	FWHM (rad)	D (Å)	χ (%)
Ch0	11.5	0.019	73	19.8
	13.2	0.014	100	
	15.1	0.018	78	
	18.8	0.003	468	
	19.7	0.140	10	
	22.7	0.027	52	
Ch2	20.3	0.142	10	18.1
	22.1	0.050	28	
Ch4	21.9	0.108	13	-
Ch9	23.7	0.116	12	-
Ch10	23.0	0.109	13	-

From Table 5.1, it can be inferred that complexation between NH_4I salt and chitosan has occurred and the addition of salt has increased the amorphousness of the chitosan membrane. The 19.8 % degree crystallinity of pure chitosan film was reduced to 18.1 % upon addition 10 wt.% NH_4I (Ch2). Due to highly amorphous film, the degree of crystallinity for sample Ch4, Ch9 and Ch10 can not be calculated. Sample Ch9 has the largest FWHM and the lowest crystallite size at amorphous halo $2\theta = 23.7^\circ$ indicating that it is the most amorphous sample. Hence the sample 55 wt.% chitosan-45 wt.% NH_4I is expected to exhibit the highest conductivity since it has the largest amorphous domain and ion conduction only occurs in the amorphous region of the polymer electrolyte.

5.3 (CHITOSAN-PVA)- NH_4I SYSTEMS

Figure 5.3 shows the X-ray diffraction patterns of pure PVA and (50 wt.% chitosan-50 wt.% PVA) blend films. The diffractogram of pure PVA exhibits a semi-crystalline structure with a peak at $2\theta = 19.5^\circ$ [Hirankumar *et al.*, 2005]. Similar observation with a halo centred at $2\theta = 20^\circ$ has been reported by Abdelaziz and Ghannam (2010). The halo centred at $2\theta = 20^\circ$ is observed to broaden and a peak at $2\theta = 11.6^\circ$ attributed to chitosan appears in diffractogram of the (50 wt.% chitosan-50 wt.% PVA) blend. A small peak at $2\theta = 16.9^\circ$ is also observed in Figure 5.3 (b). The shifting the peak from $2\theta = 19.5^\circ$ to $2\theta = 20^\circ$ and the appearance of peak at $2\theta = 16.9^\circ$ in diffractogram of the (50 wt.% chitosan-50 wt.% PVA) blend is due to interaction between chitosan and PVA which is confirmed by FTIR studies.

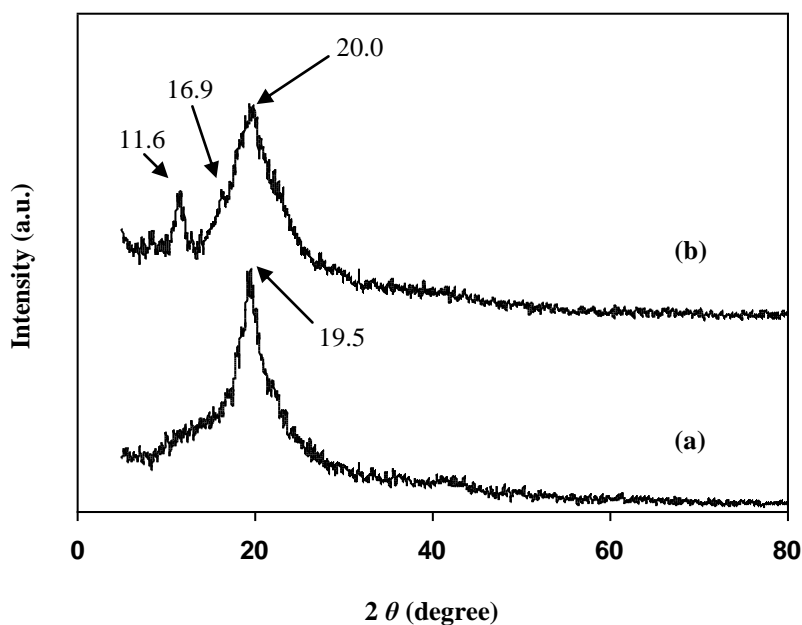


Figure 5.3: X-ray diffraction patterns of (a) pure PVA and (b) (50 wt.% chitosan-50 wt.% PVA) films

The X-ray diffraction patterns of (chitosan-PVA)- NH_4I electrolytes and NH_4I salt are shown in Figure 5.4. The crystalline peaks of NH_4I salt are observed at $2\theta = 21.1^\circ$, 24.7° , 34.8° , 41.2° , 43.2° , 50.5° , 55.0° , 56.4° , 62.5° , 67.0° and 77.9° . The XRD patterns of (chitosan-PVA)- NH_4I show that the samples are highly amorphous until (27.5 wt.% chitosan-27.5 wt. % PVA)-45 wt.% NH_4I (CV5). At (22.0 wt.% chitosan-33.0 wt. % PVA)-45 wt.% NH_4I (CV6), some crystalline peaks have appeared in the diffractogram at $2\theta = 21.1^\circ$, 24.5° , 34.9° , 41.2° , 55.1° , 56.6° and 62.6° . These peaks are attributed to NH_4I salt. The recrystallization of salt out of the polymer host may lead to loss of mobile ions resulting in the sample to exhibit low conductivity. It may also be inferred that the host is unable to solvate all the salt at PVA concentration of 33 wt.% and above. Hence, a substantial portion of the salt is not entrapped in the polymer host and is deposited on the surface when the film has formed. Intensity of the NH_4I peaks increases and more peaks are observed at $2\theta = 43.1^\circ$, 50.2° and 66.9° for samples with 44 wt.% PVA (CV8) content.

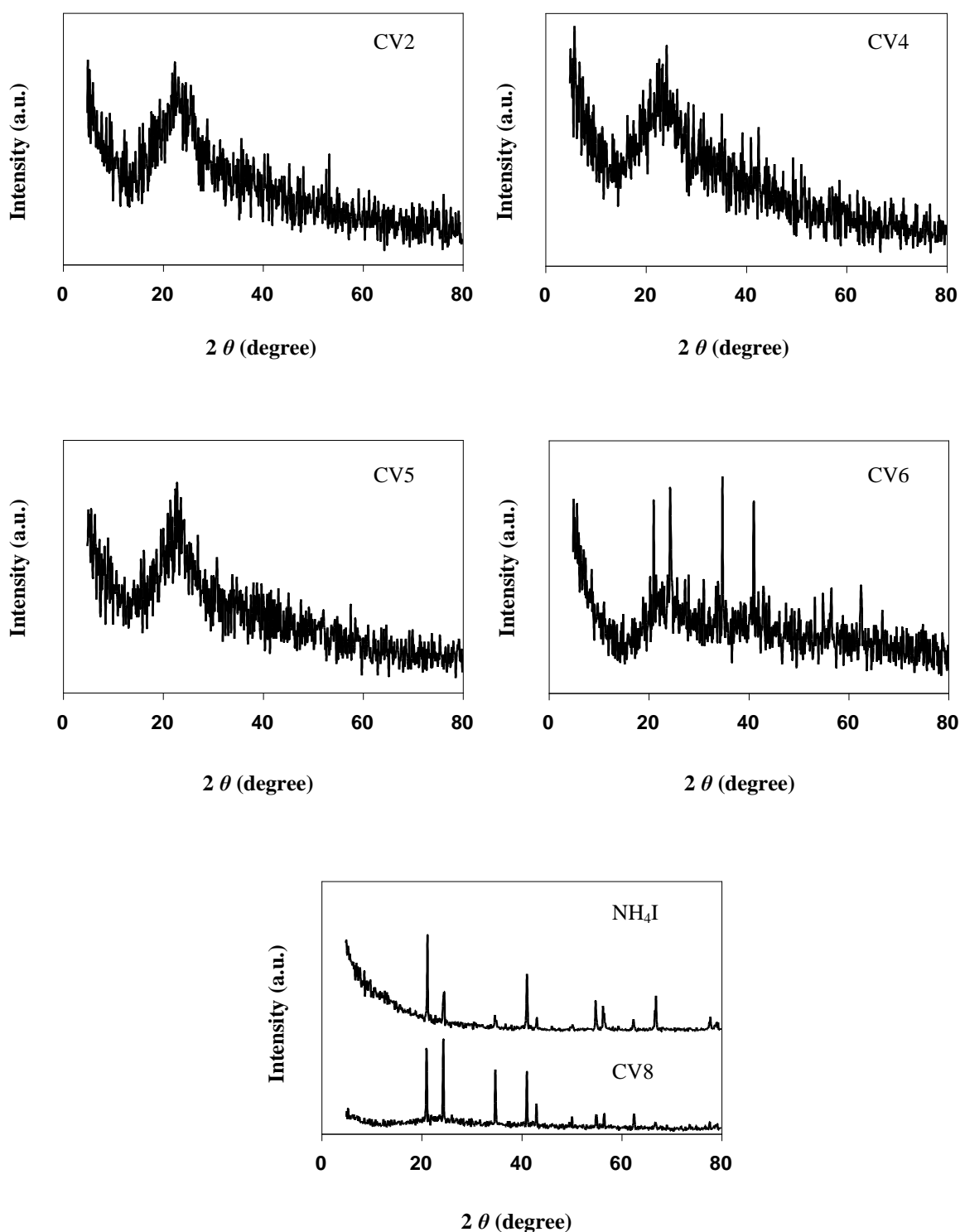
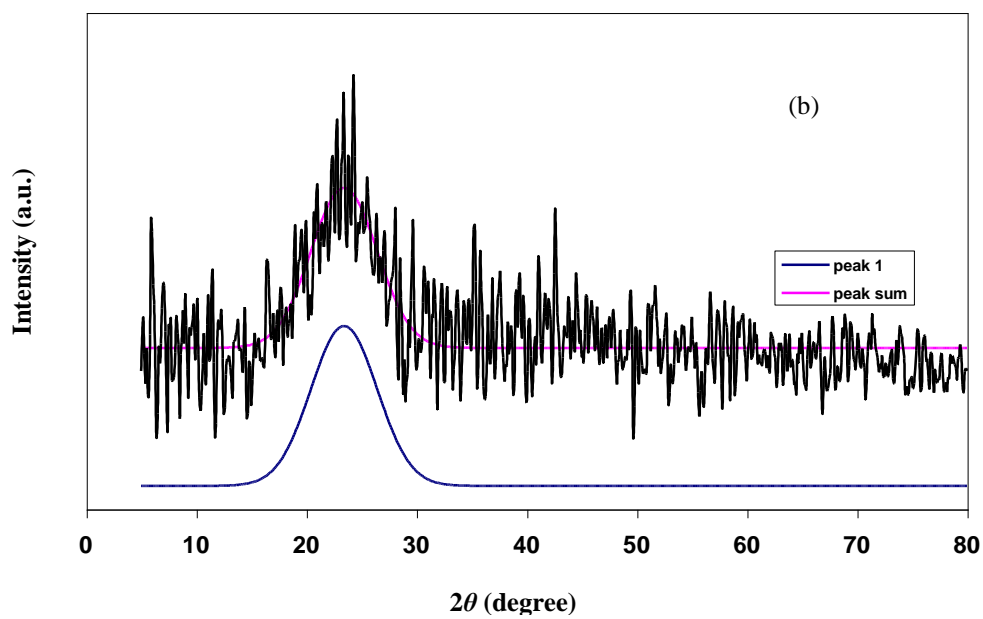
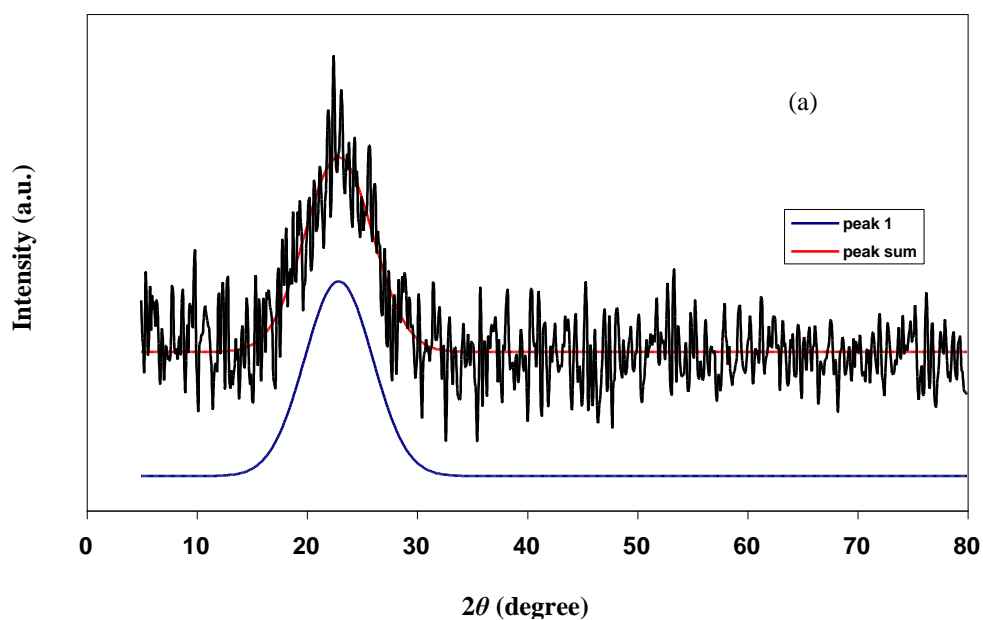


Figure 5.4: X-ray diffraction patterns of (chitosan-PVA)-NH₄I electrolytes containing (44.0 wt.% chitosan-11.0 wt.% PVA)-45 wt.% NH₄I (CV2), (33.0 wt.% chitosan-22 wt.% PVA)-45 wt.% NH₄I (CV4), (27.5 wt.% chitosan-27.5 wt.% PVA)-45 wt.% NH₄I (CV5), (22 wt.% chitosan-33 wt.% PVA)-45 wt.% NH₄I (CV6), (11 wt.% chitosan-44 wt.% PVA)-45 wt.% NH₄I (CV8) and NH₄I salt

In order to determine which of the three samples CV2, CV4, and CV5 is the most amorphous, gaussian fitting using the Origin 8 software has been carried out and is shown in Figure 5.5.



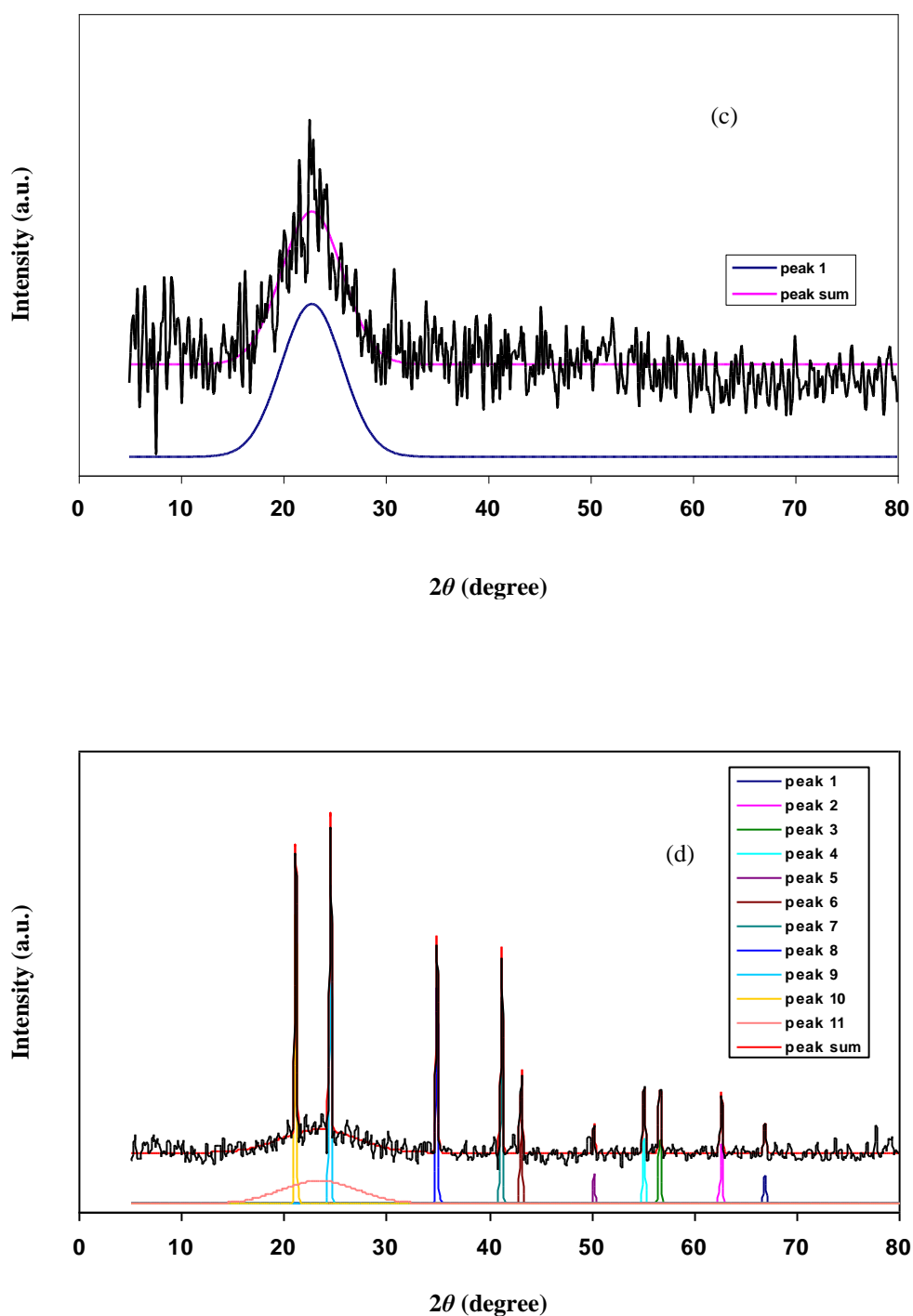


Figure 5.5: Gaussian fitting of XRD for (chitosan-PVA)-NH₄I electrolytes containing (a) (44.0 wt.% chitosan-11.0 wt.% PVA)-45 wt.% NH₄I (CV2), (b) (33.0 wt.% chitosan-22 wt.% PVA)-45 wt.% NH₄I (CV4), (c) (27.5 wt.% chitosan-27.5 wt.% PVA)-45 wt.% NH₄I (CV5) and (d) (11 wt.% chitosan-44 wt.% PVA)-45 wt.% NH₄I (CV8)

From Figure 5.5, the center of amorphous halo is observed at $2\theta = 22.9^\circ$ for CV2, 23.4° for CV4 and 22.8° for CV5. It can be clearly seen that no additional peaks appear in

addition to the amorphous halo for the three samples. The shifting of the amorphous halo peak indicated that some complexation occurred between NH_4I and chitosan-PVA blend as confirmed by FTIR spectrum. To determine the amorphousness precisely between the three samples, FWHM and crystallite size, D was calculated from the Origin 8 software.

Table 5.2 lists the FWHM and crystallite size for samples designated as CV2, CV4, CV5 and CV8. It can be observed that the FWHM and crystallite size value is almost the same for the CV2, CV4 and CV5. The degree of crystallinity of the CV8 electrolyte is 41.7 %. From Figure 5.4 and Table 5.2, the highest conductivity sample in this system is expected to be CV2, CV4 and CV5.

Table 5.2: FWHM, D and χ (%) for selected (chitosan-PVA)- NH_4I electrolytes

Electrolytes	2θ (degree)	FWHM (rad)	D (Å)	χ (%)
CV2	22.9	0.106	13.3	-
CV4	23.4	0.105	13.5	-
CV5	22.8	0.104	13.6	-
CV8	21.1	0.004	353	41.7
	23.4	0.129	11	
	24.5	0.003	473	
	34.9	0.004	363	
	41.2	0.003	494	
	43.1	0.003	497	
	50.2	0.003	510	
	55.1	0.004	391	
	56.6	0.004	394	
	62.6	0.004	406	
66.9	0.004	415		

5.4 (CHITOSAN-PEO)-NH₄I SYSTEMS

Fig. 5.6 shows the X-ray diffraction patterns of (30 wt.% chitosan-70 wt.% PEO) blend and pure PEO film. The pure PEO film exhibits two clear peaks at $2\theta = 19.1^\circ$ and 23.2° . From the figure, weaker crystalline peaks can be observed at $2\theta = 13.4^\circ$, 15.4° , 26.7° , and 36.3° . The PEO blended with 30 wt.% chitosan is inferred to be more amorphous since the crystalline peak at $2\theta = 19.1^\circ$ has disappeared in the diffractogram of the (30 wt.% chitosan-70 wt.% PEO) sample.

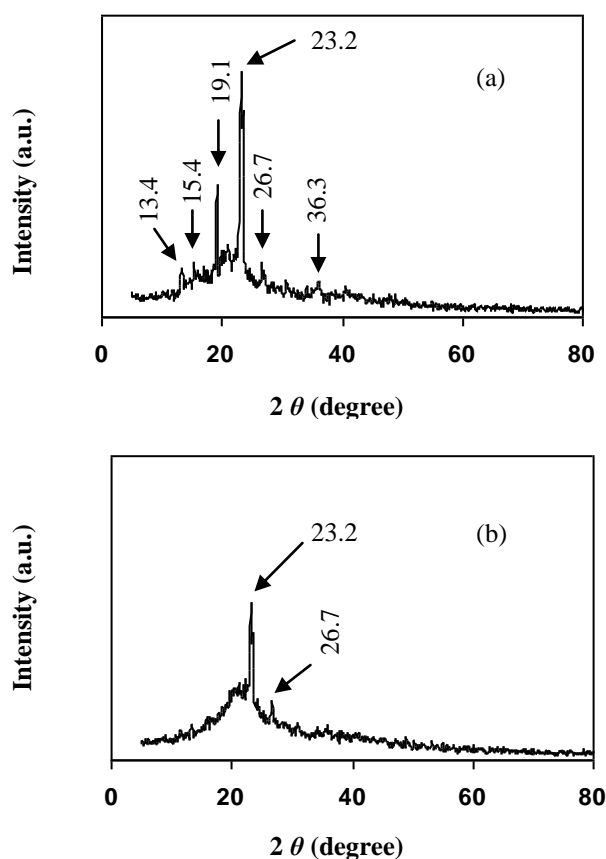


Figure 5.6: X-ray diffraction patterns of (a) pure PEO and (b) (30 wt.% chitosan-70 wt.% PEO) films

The X-ray diffraction patterns of the (chitosan-PEO)-NH₄I electrolytes are shown in Figure 5.7. The diffractograms of (chitosan-PEO)-NH₄I electrolytes show no presence of major peaks. This indicates that the (chitosan-PEO)-NH₄I electrolytes are amorphous

in nature. However, a small peak can still be seen at $2\theta = 13.0^\circ$ in the XRD patterns of electrolyte blends designated as CEO2, CEO3, CEO4 and CEO7. The addition of NH_4I salt to the (30 wt.% chitosan-70 wt.% PEO) blend clearly reduces the crystallinity of the blend as shown in the diffractogram of (16.5 wt.% chitosan-38.5 wt.% PEO)-45 wt.% NH_4I (CEO7) electrolyte in Figure 5.7.

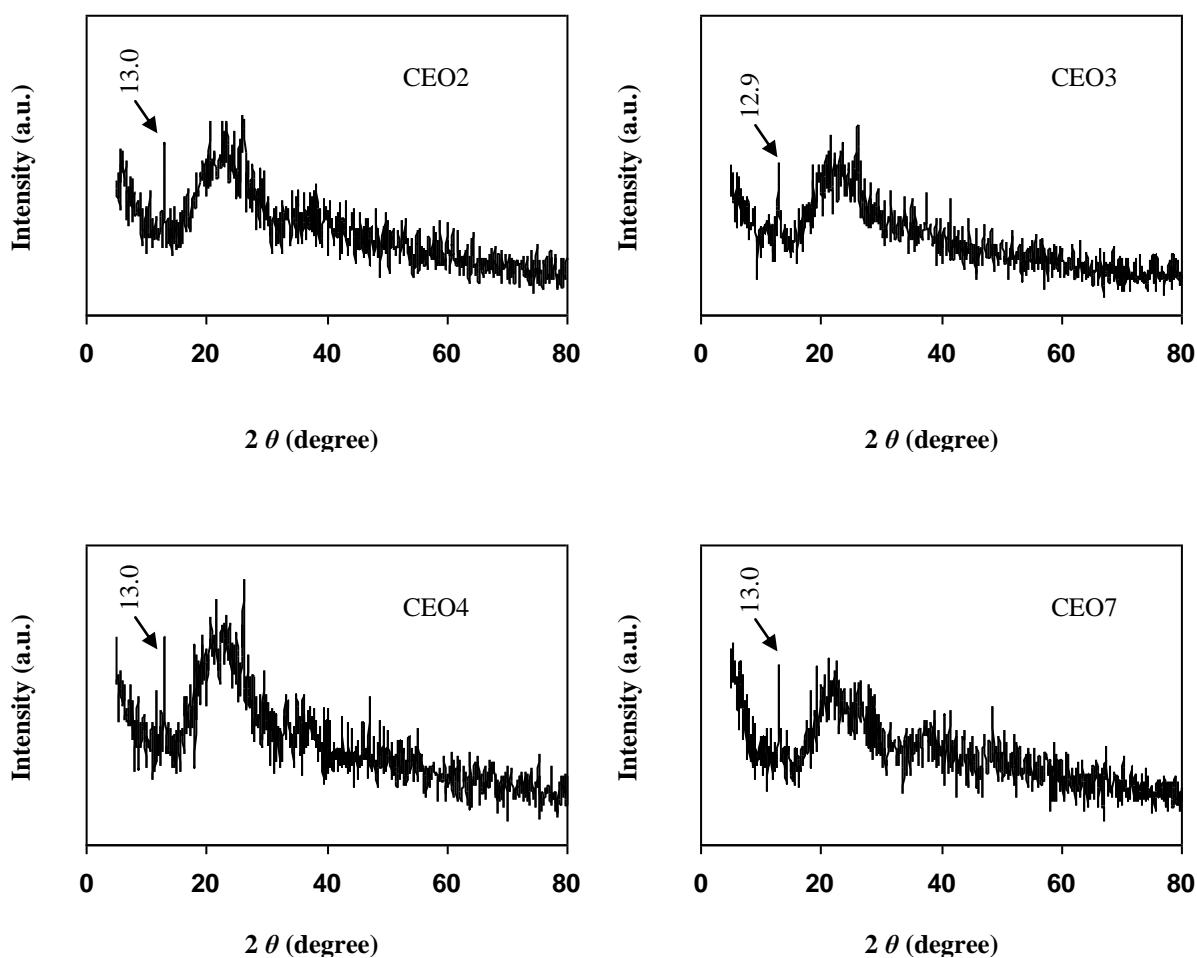
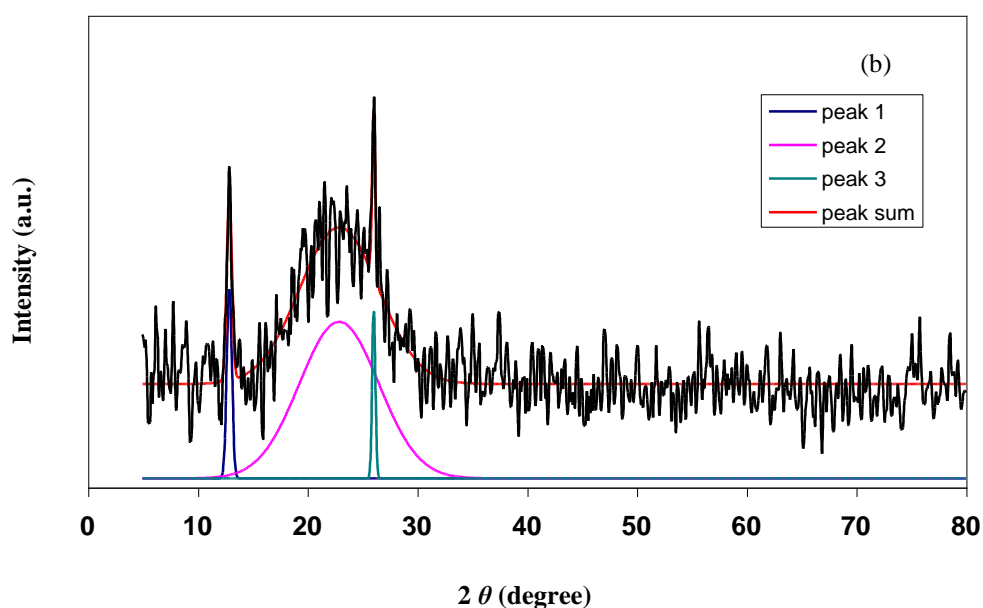
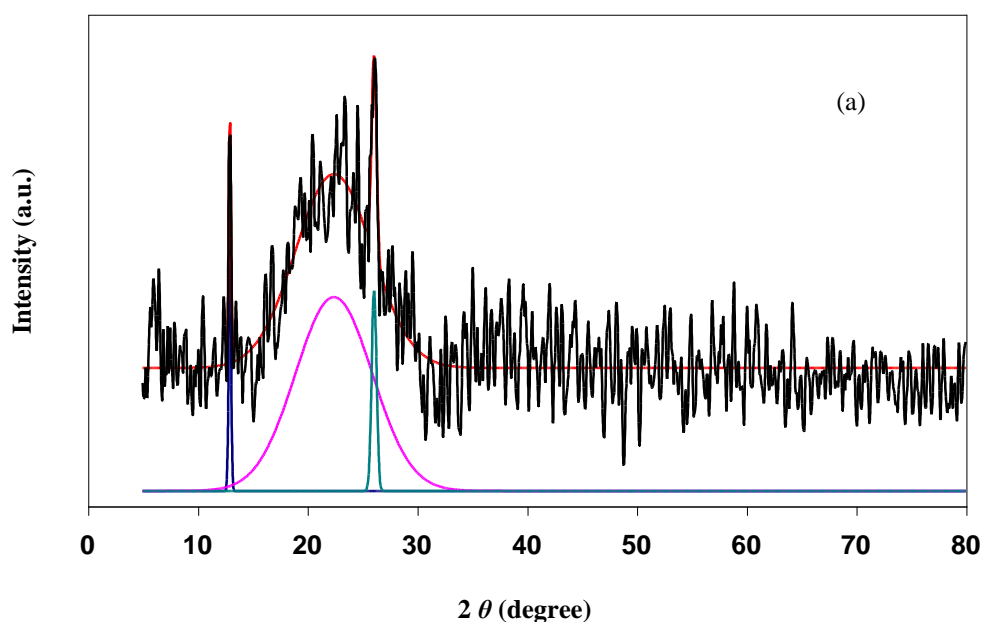


Figure 5.7: X-ray diffraction patterns of (chitosan-PEO)- NH_4I electrolytes containing (44 wt.% chitosan-11 wt.% PEO)-45 wt.% NH_4I (CEO2), (38.5 wt.% chitosan-16.5 wt.% PEO)-45 wt.% NH_4I (CEO3), (33 wt.% chitosan-22 wt.% PEO)-45 wt.% NH_4I (CEO4), and (16.5 wt.% chitosan-38.5 wt.% PEO)-45 wt.% NH_4I (CEO7)

Figure 5.8 depicts the results of gaussian fitting on (44 wt.% chitosan-11 wt.% PEO)-45 wt.% NH_4I (CEO2), (38.5 wt.% chitosan-16.5 wt.% PEO)-45 wt.% NH_4I (CEO3), (33

wt.% chitosan-22 wt.% PEO)-45 wt.% NH_4I (CEO4) and (16.5 wt.% chitosan-38.5 wt.% PEO)-45 wt.% NH_4I (CEO7) electrolytes. A crystalline peak at $2\theta = 26.1^\circ$ can be observed for sample designated CEO2, CEO3 and CEO4 apart from the crystalline peak at $2\theta = 13.0^\circ$ and amorphous halo centred between 22° and 23° . The peak at $2\theta = 26.1^\circ$ is absent in the diffractograms of CEO7.



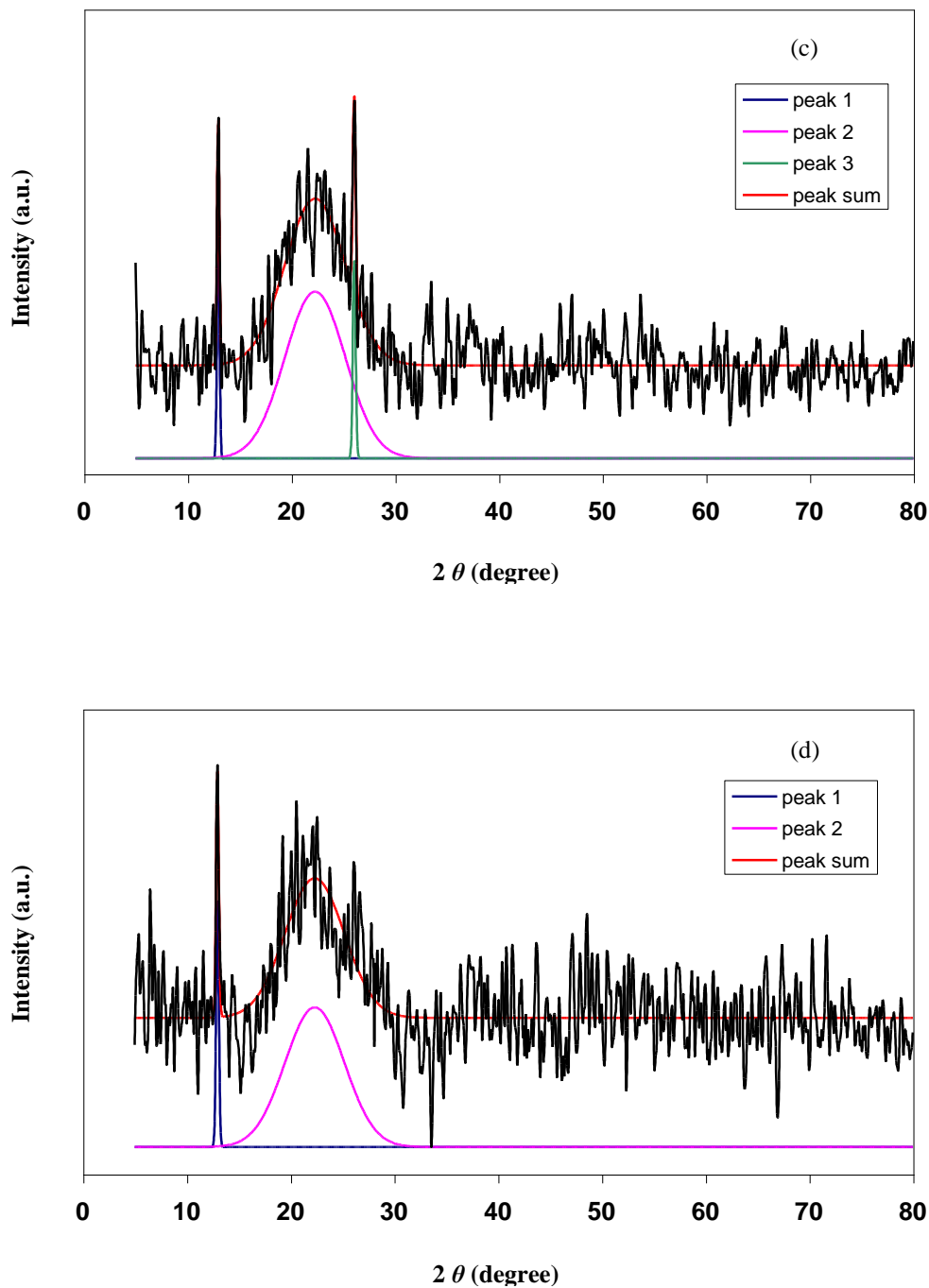


Figure 5.8: Gaussian fitting of XRD for (chitosan-PEO)-NH₄I electrolytes containing (a) (44.0 wt.% chitosan-11.0 wt.% PEO)-45 wt.% NH₄I (CEO2) (b) (38.5 wt.% chitosan-16.5 wt.% PEO)-45 wt.% NH₄I (CEO3), (c) (30 wt.% chitosan-22 wt.% PEO)-45 wt.% NH₄I (CEO4) and (d) (16.5 wt.% chitosan-38.5 wt.% PEO)-45 wt.% NH₄I (CEO7)

The FWHM, crystallite size, D and χ (%) values for samples CEO2, CEO3, CEO4 and CEO7 are tabulated in Table 5.3.

Table 5.3: FWHM, D and χ (%) for selected (chitosan-PEO)-NH₄I electrolytes

Electrolyte	2θ (degree)	FWHM (rad)	D (Å)	χ (%)
CEO2	13.0	0.004	349	9.6
	22.4	0.122	11	
	26.1	0.008	178	
CEO3	12.9	0.008	174	11.0
	22.9	0.126	11	
	26.1	0.005	285	
CEO4	13.0	0.004	349	10.2
	22.3	0.101	14	
	26.1	0.005	285	
CEO7	13.0	0.005	279	7.6
	22.4	0.100	14	

The sample designated CEO7 is the most amorphous film compared to the CEO2, CEO3 and CEO4 since it has lesser crystalline peaks and lower degree of crystallinity although it shows larger crystallite size compared to CEO2 and CEO3. Hence, CEO7 is expected to exhibit the highest ionic conductivity at room temperature.

5.5 CHITOSAN-NH₄I-IL SYSTEMS

Figure 5.9 depicts the X-ray diffraction patterns of chitosan-NH₄I-IL electrolytes. It can be observed that the chitosan-NH₄I-IL electrolytes are highly amorphous. There are no significant changes in the diffractogram of the chitosan-NH₄I electrolytes with the incorporation of 1-butyl-3-methylimidazolium iodide ionic liquid.

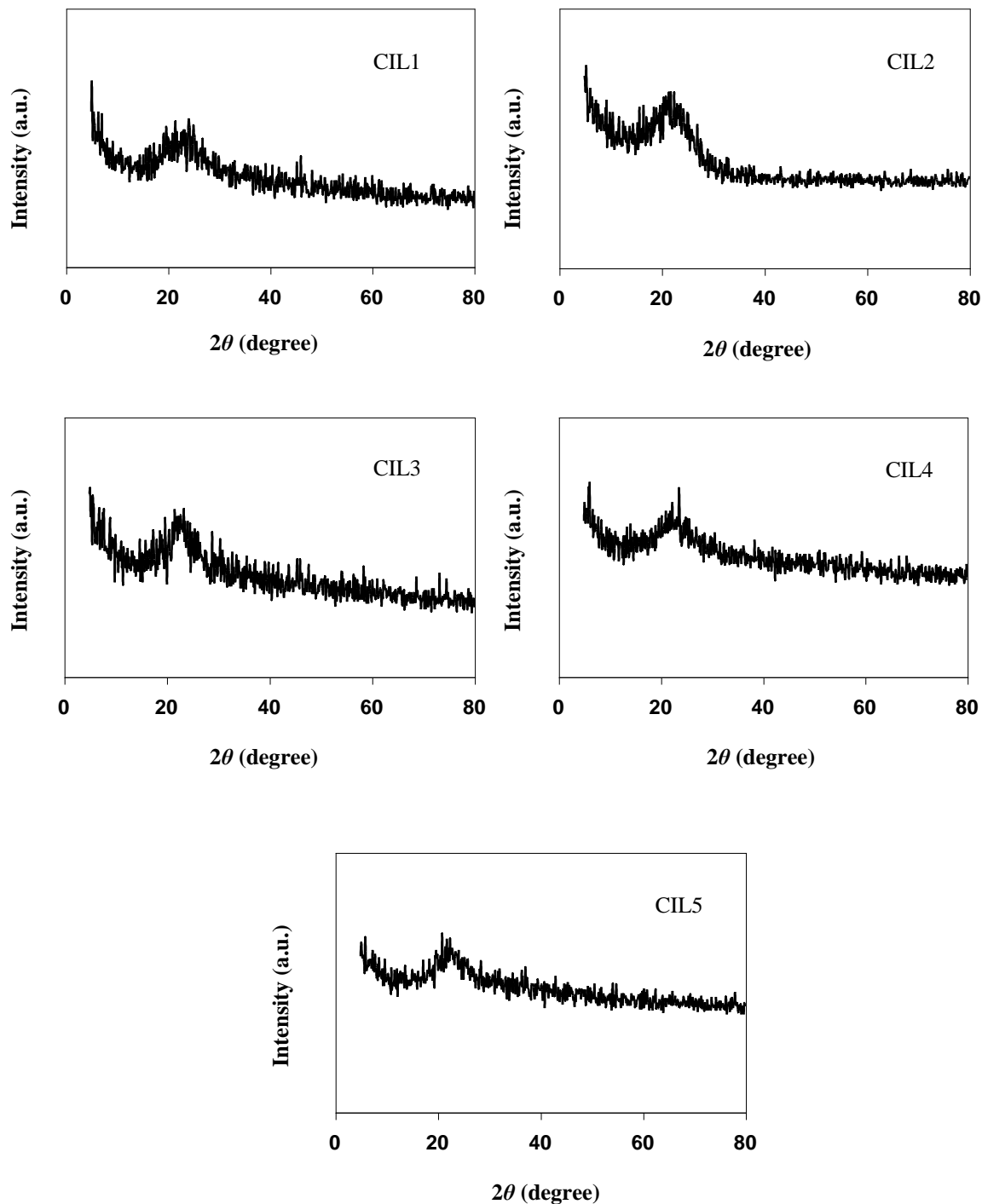
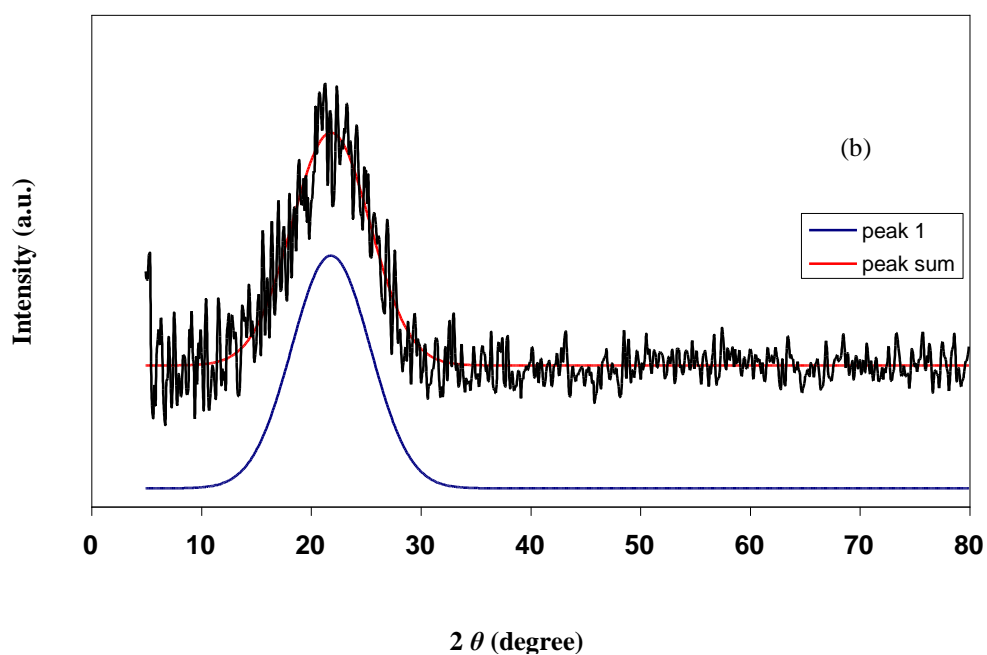
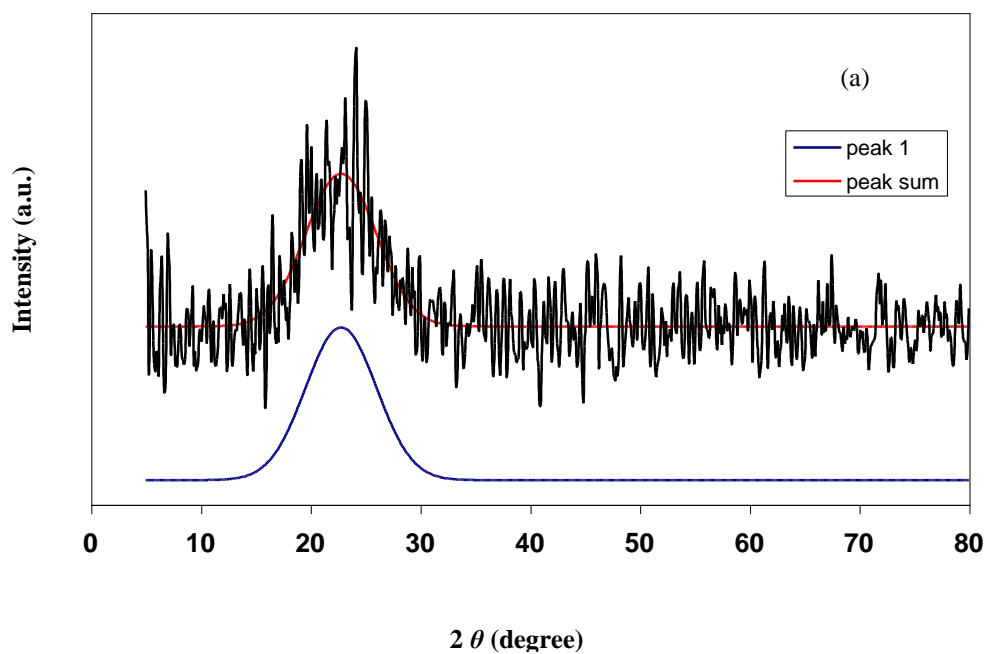


Figure 5.9: X-ray diffraction patterns of chitosan-NH₄I-IL electrolytes containing 49.5 wt.% chitosan-40.5 wt.% NH₄I-10 wt.% IL (CIL1), 44.0 wt.% chitosan-36.0 wt.% NH₄I-20 wt.% IL (CIL2), (38.5 wt.% chitosan-31.5 wt.% NH₄I-30 wt.% IL (CIL3), 33 wt.% chitosan-27 wt.% NH₄I-40 wt.% IL (CIL4) and (d) 27.5 wt.% chitosan-22.5 wt.% NH₄I-50 wt.% IL (CIL5)

Figure 5.10 depicts the results of gaussian fitting on 49.5 wt.% chitosan-40.5 wt.% NH_4I -10 wt.% IL, 44.0 wt.% chitosan-36.0 wt.% NH_4I -20 wt.% IL, 38.5 wt.% chitosan-31.5 wt.% NH_4I -30 wt.% IL and 27.5 wt.% chitosan-22.5 wt.% NH_4I -50 wt.% IL electrolytes.



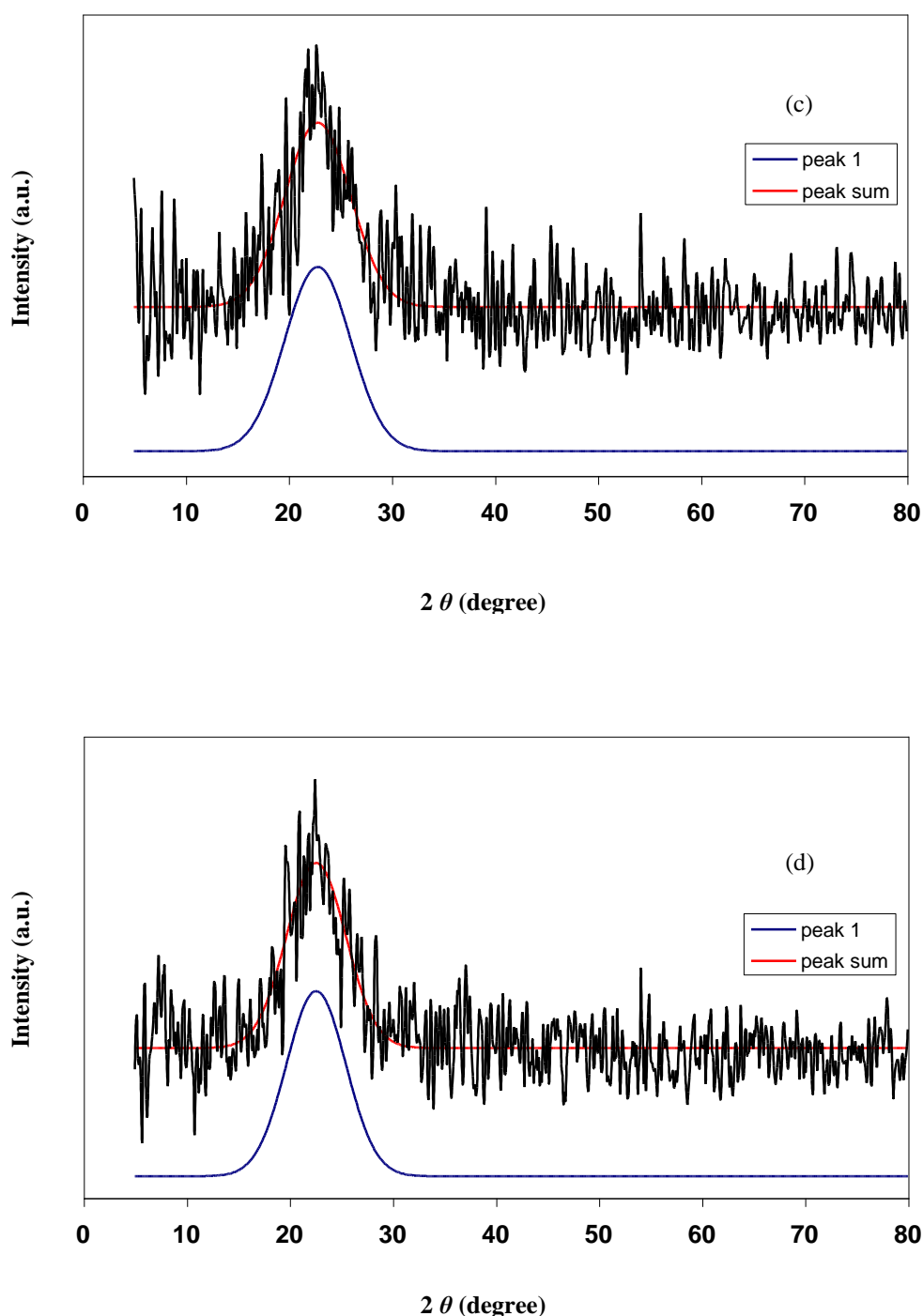


Figure 5.10: Gaussian fitting of XRD for chitosan-NH₄I-IL electrolytes containing (a) 49.5 wt.% chitosan-40.5 wt.% NH₄I-10 wt.% IL (CIL1), (b) 44.0 wt.% chitosan-36.0 wt.% NH₄I-20 wt.% IL (CIL2), (c) 38.5 wt.% chitosan-31.5 wt.% NH₄I-30 wt.% IL (CIL3) and (d) 27.5 wt.% chitosan-22.5 wt.% NH₄I-50 wt.% IL (CIL5)

It may be inferred, since there are no crystalline peaks from the deconvolution of the amorphous hump, that the addition of IL into the chitosan-salt samples has disrupted

most of the crystalline peaks attributed to chitosan. For more details, the full width at half maximum (FWHM) and crystallite size of the amorphous halo has been calculated in Table 5.4. The sample designated CIL2 and CIL4 is expected to exhibit the highest conductivity sample since both has large FWHM and small crystallite size.

Table 5.4: FWHM and D for selected chitosan-NH₄I-IL electrolytes

Electrolytes	2θ (degree)	FWHM (rad)	D (Å)
CIL1	22.8	0.113	12
CIL2	21.9	0.124	11
CIL3	22.8	0.111	12
CIL4	23.0	0.122	11
CIL5	22.6	0.101	14

5.6 SUMMARY

From X-ray diffraction studies, the semicrystalline nature of chitosan film becomes more amorphous with addition of NH₄I. The expected highest conducting sample in the chitosan-NH₄I system is Ch9 (55 wt.% chitosan-45 wt.% NH₄I) since it is the most amorphous film. The shifts for the centre peak of pure chitosan at $2\theta = 22.7^\circ$ to $2\theta = 23.7^\circ$ shows that complexation between NH₄I and chitosan has been occurred. The amorphousness of Ch9 sample is decreased with addition of poly(vinyl alcohol), PVA. Upon deconvolution of the diffractogram for the (chitosan-PEO)-NH₄I sample designated CEO7 has less one crystalline peak and is inferred to be the most amorphous film that should exhibit the highest conducting sample in the system.