

CHAPTER 5

RESULTS OF X-RAY DIFFRACTION SPECTROSCOPY

5.1 Introduction

XRD is a powerful technique to obtain information of a polymeric electrolyte with regards to the material and its nature (West, 1987). The XRD patterns can help to identify the structure of the crystalline form and the crystalline dimensions of the electrolyte material. They can also be used to help in the investigation of the occurrence of polymer-salt complexation. If complexation occurs in the crystalline phase, then (i) new crystalline peaks are observed apart from pure polymer and salt peaks or/and (ii) peaks corresponding to the pure polymer and salt are shifted from their original 2θ position. If no new peaks or any major changes in XRD are observed, then either complexation has occurred in the amorphous phase or complexation has not occurred at all (Sekhon et al., 1995).

5.2 XRD of pure PEO and PEO-LiI complexes

The macroscopic structure of the polymeric composite was examined by XRD analysis, which was performed at room temperature. In Fig 5.1 XRD patterns for pure PEO film and PEO-LiI solid electrolytes are shown. The peak at $2\theta = 19^\circ$ is attributed to the pure crystalline polymer (Kalita et al., 2007). It is obvious from the intensity of the peak that an addition of lithium salt reduces the PEO crystalline structure. The XRD peak visible at about 23° is attributed to the PEO/LiI complex suggesting a rapid decrease of the PEO crystallinity resulting from the coordination interactions between the ether oxygen atoms of PEO and Li^+ (Xi et al., 2005).

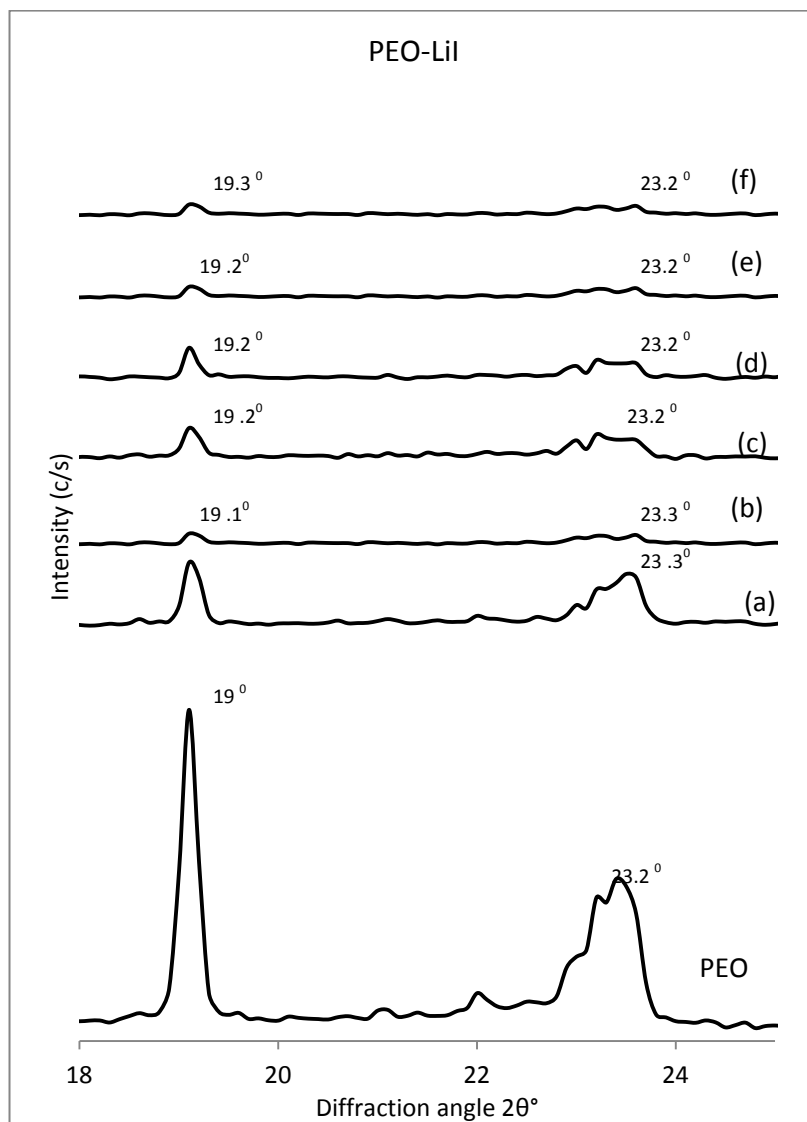
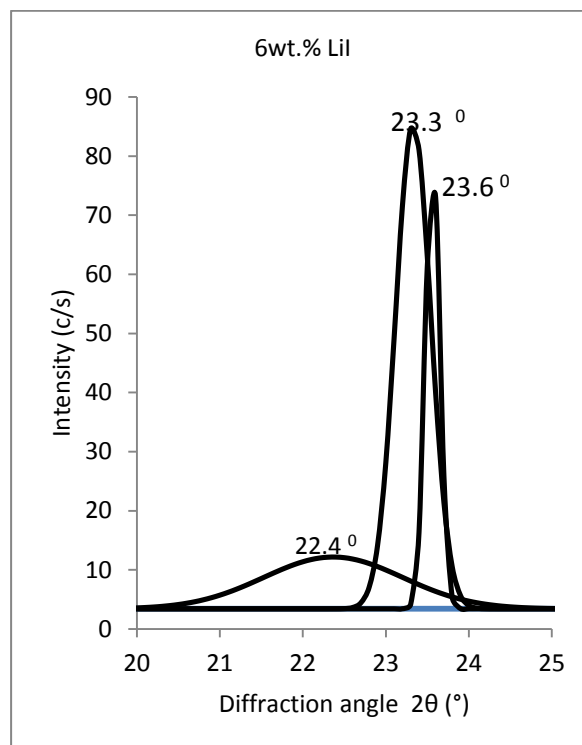
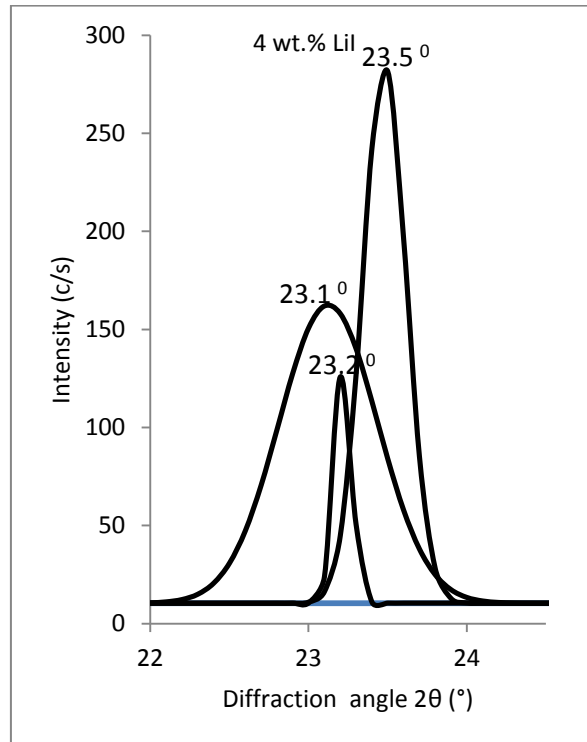


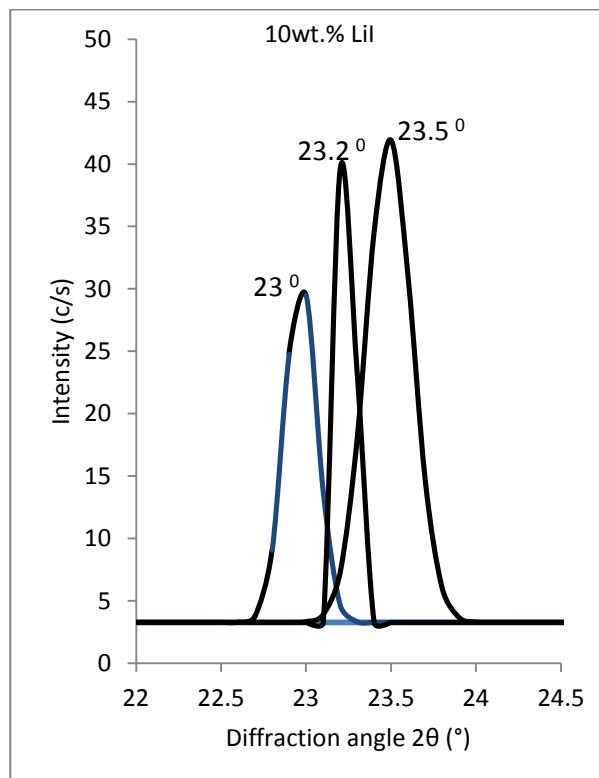
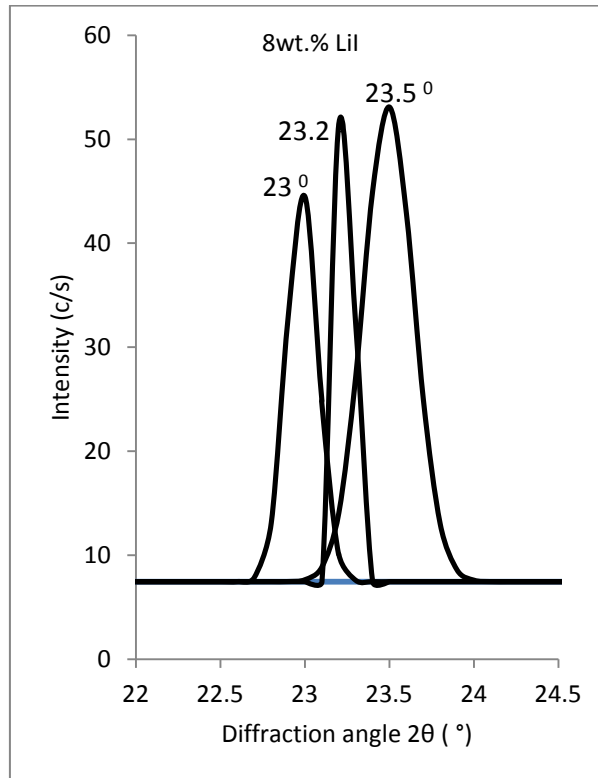
Figure 5.1: XRD patterns of pure PEO film and PEO with different wt.% of LiI (a) PEO- 4wt.% LiI, (b) PEO- 6wt.% LiI, (c) PEO- 8wt.% LiI (d) PEO-10wt.% LiI, (e) PEO-12wt.% LiI and (f) PEO-14wt.% LiI

From Figure 5.1, it is very clear that when the concentration of salt increases the crystallinity of polymer host decreases. For the pure PEO the peak at 19° gets shifted to 19.3° and the intensity decreases by the addition of different wt. % of LiI salt. This shows on addition of LiI salt into the polymer, a good complexation is formed between Li^+ ions and the oxygen atoms in the PEO, resulting in the reduction of crystallinity of the polymer electrolyte associated with the enhancement of the amorphous phase (Sreekanth et al., 1999, Kuila et al., 2007, and Mohan et al., 2005). The XRD pattern of

PEO is composed of two strong Bragg peaks at 19° and 23° . In Fig 5.1, the intensities of these peaks at 19° and 23° decreases as the salt content increases. The less intense and differing in width of these peaks show that complexation has occurred between LiI and the polymer (Greenbaum et al., 1997, Golodnitsky et al., 2002). When the Li salt is incorporated into the PEO matrix, the diffraction peaks of the resulting polymer electrolytes become weaker suggesting a decrease of PEO crystallinity. In addition, all the peaks corresponding to the PEO polymer are also present in the complexed PEO film indicating the presence of both crystalline and amorphous domain in the complexed PEO (Mohan et al., 2005). The study shows that for some samples, the peak maximum of peak 23° is slightly shifted and/or the peak can be split. This phenomenon is related to the formation of the crystalline polymer salt complex. Kalita et al., (2007) have studied for PEO-LiTf and PEO-LiI systems. The results have shown that the LiTf containing samples are generally less crystalline than the ones doped with LiI. However, no additional peaks corresponding to LiI are observed in PEO complexes, indicating the absence of any uncomplexed lithium salt.

From Figure 5.1, the peak at 23° splits into three. On closer examination of the peak at 23° using Origin software the splitting pattern are as shown in Figure 5.2 below.





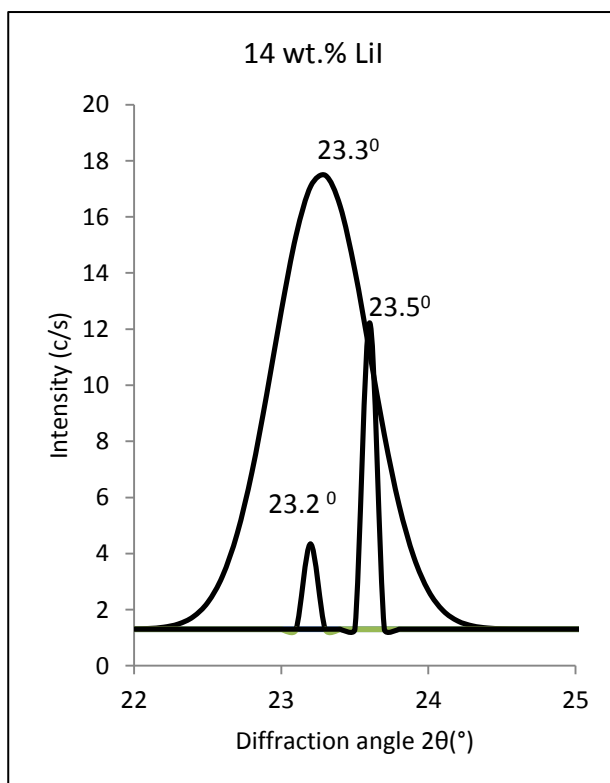
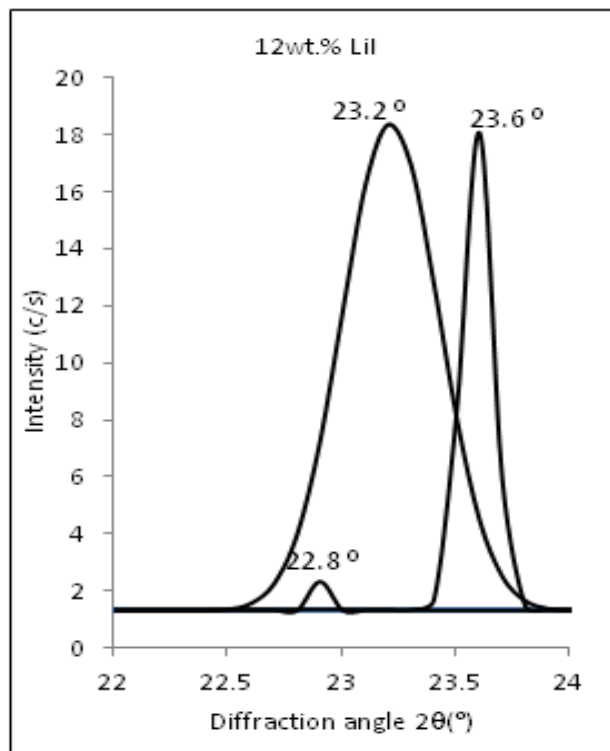


Figure 5.2: XRD patterns of pure PEO film and PEO with different wt. % of LiI. (a) PEO- 4% LiI, (b) PEO- 6% LiI, (c) PEO- 8% LiI (d) PEO-10% LiI, (e) PEO-12% LiI and (f) PEO-14% LiI

Fig 5.3 shows the percentage of crystallinity peak at 19° , calculated using Origin software for various PEO-LiI systems. PEO incorporated with 10 wt. % LiI salt shows the lowest percentage of crystallinity therefore this sample is the most amorphous and should exhibit the highest conductivity at room temperature. This is the same trend with that obtained from FTIR results.

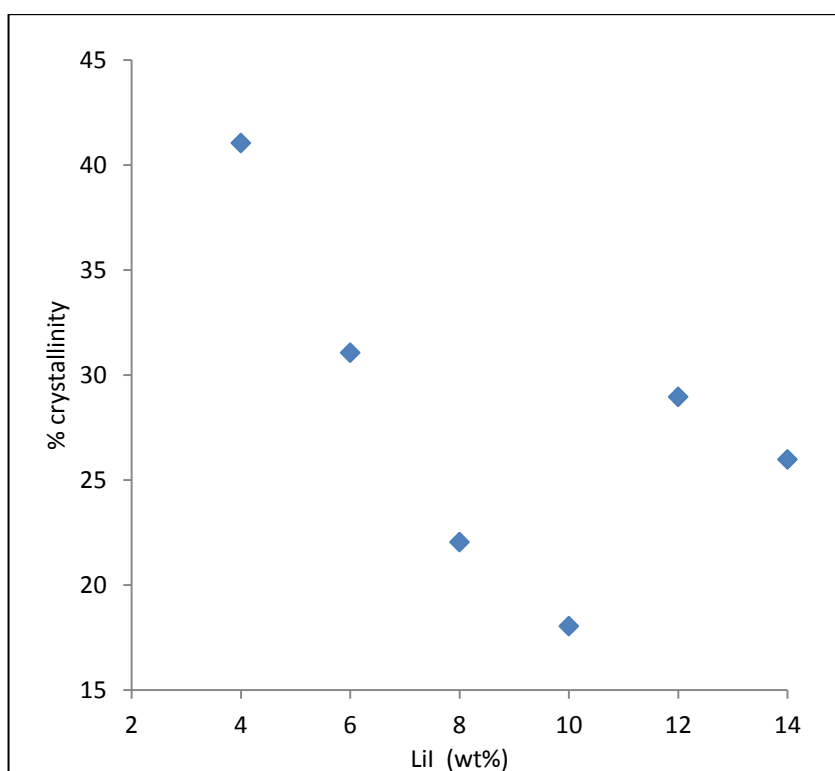


Figure 5.3: Shows the % of crystallinity of LiI (4 wt.%-14 wt.%) at peak 19°

Figure 5.4 represents the percentage of crystallinity of peak at 23° for different weight percentages varying from 4wt.% to 14 wt.% of LiI. At 10 wt.% of LiI shows the lowest percentage of crystallinity is another proof for the amorphous nature of the system. The crystallinity of the peak is calculated using the Origin software.

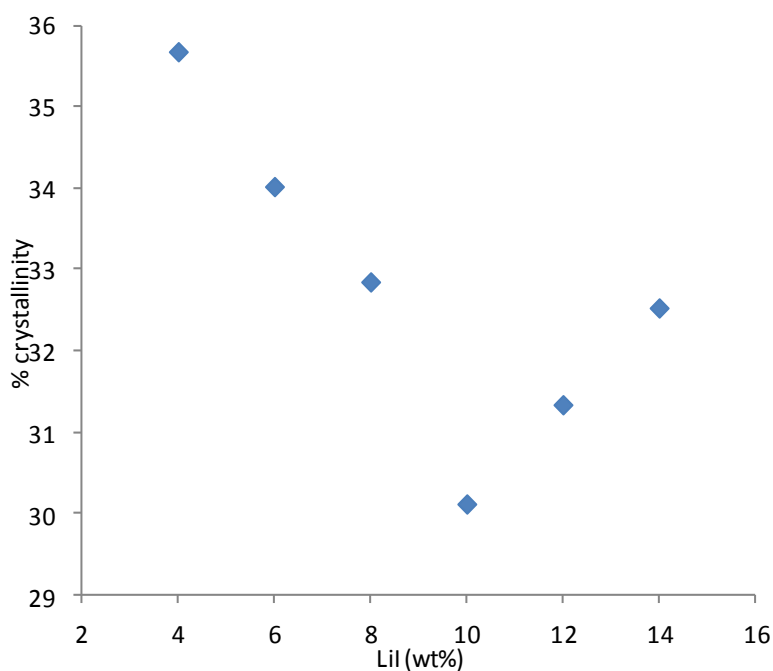


Figure 5.4: Percentage of crystallinity of LiI (4 wt.%-14 wt.%) at $2\theta = 23^\circ$

5.3 XRD of PEO-LiI- Al_2O_3 composite

Fig 5.5 shows the XRD patterns after the addition of different weight percentages Al_2O_3 inorganic filler to the highest conducting PEO-LiI system. The characteristic peak at $2\theta = 23^\circ$ has become broader suggesting a reduction in PEO crystallinity (Xi et.al.2005). Moreover, Al_2O_3 may provide more Lewis acid-base interactions with Li^+ and PEO chains yielding new electrolyte properties (Golodnisky et.al.,1998, Ardel et.al., 1996). This complexation agrees well with the FTIR results.

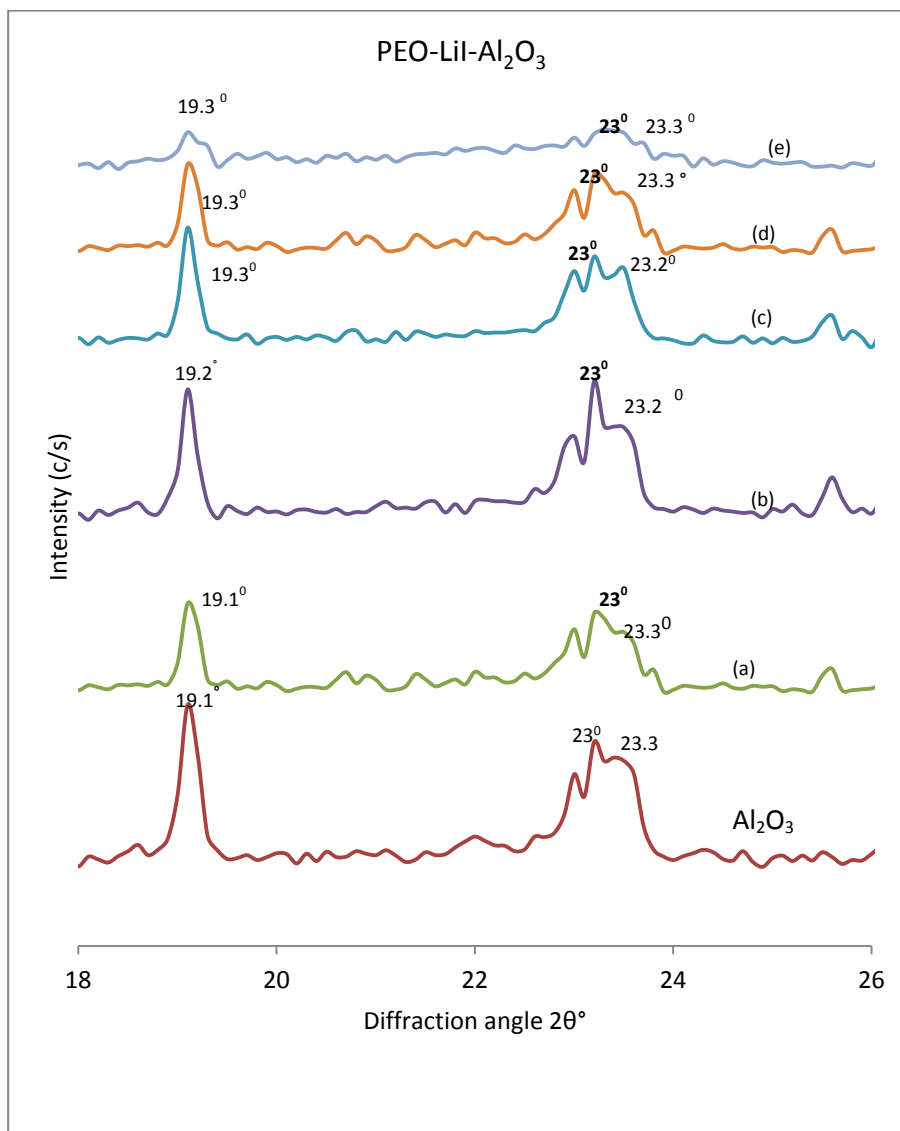
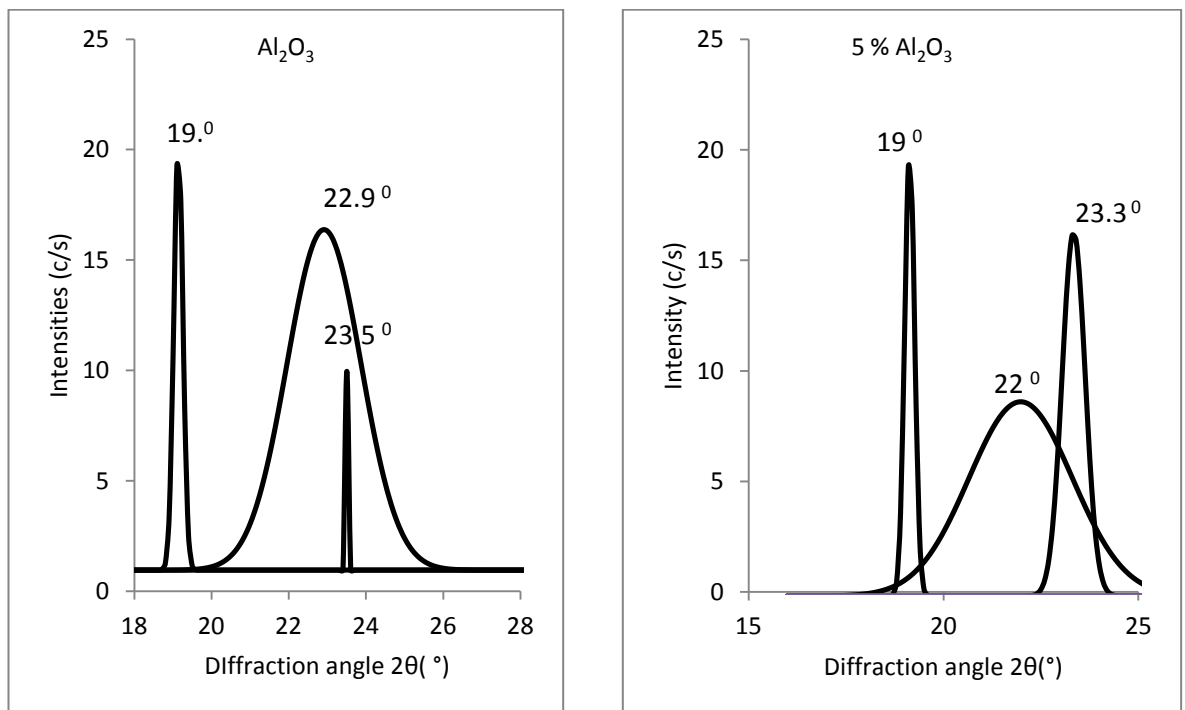


Figure 5.5: XRD pure Al_2O_3 and $\text{PEO-LiI-Al}_2\text{O}_3$, (a) 85.5 wt.% PEO: 9.5wt.% LiI:5 wt.% Al_2O_3 , (b) 81.0wt.% PEO: 9wt.%LiI:10wt.% Al_2O_3 , (c) 76.5wt.% PEO :8.5wt.% LiI:15 wt.% Al_2O_3 , (d) 72.0wt. %PEO : 8wt.% LiI:20wt.% Al_2O_3 , (e) 67.5 wt.% PEO : 7.5 wt.% LiI : 25 wt.% Al_2O_3

In the XRD patterns of Fig 5.5, intensity of the peaks at 19° and 23° are getting reduced. Hence, an increase in the concentration of Al_2O_3 from 5 wt. % to 25 wt. % revealed a corresponding decrease in the intensities of the observed peaks pointing towards the fact that complexation between PEO and the Al_2O_3 takes place. The incorporation of excess Al_2O_3 would eventually lead to the phase separation of alumina from solid polymer electrolytes. The occurrence of phase separation may cause a loss of

conducting pathways responding to their low conductivity, because ions could not cross the filler-polymer interface (Kao et al., 2005)

Figure 5.6 depicts the deconvoluted peak at 23° of PEO system with different weight percentages of LiI. It may also be seen from Figure that the pattern obtained for the nanocomposite polymer electrolytes has not revealed any new peaks in the range of $2\theta = 25^\circ$ suggesting the absence of any new crystalline complex (Hashmi et al.,(1990) and Anantha et al.,(2005)).



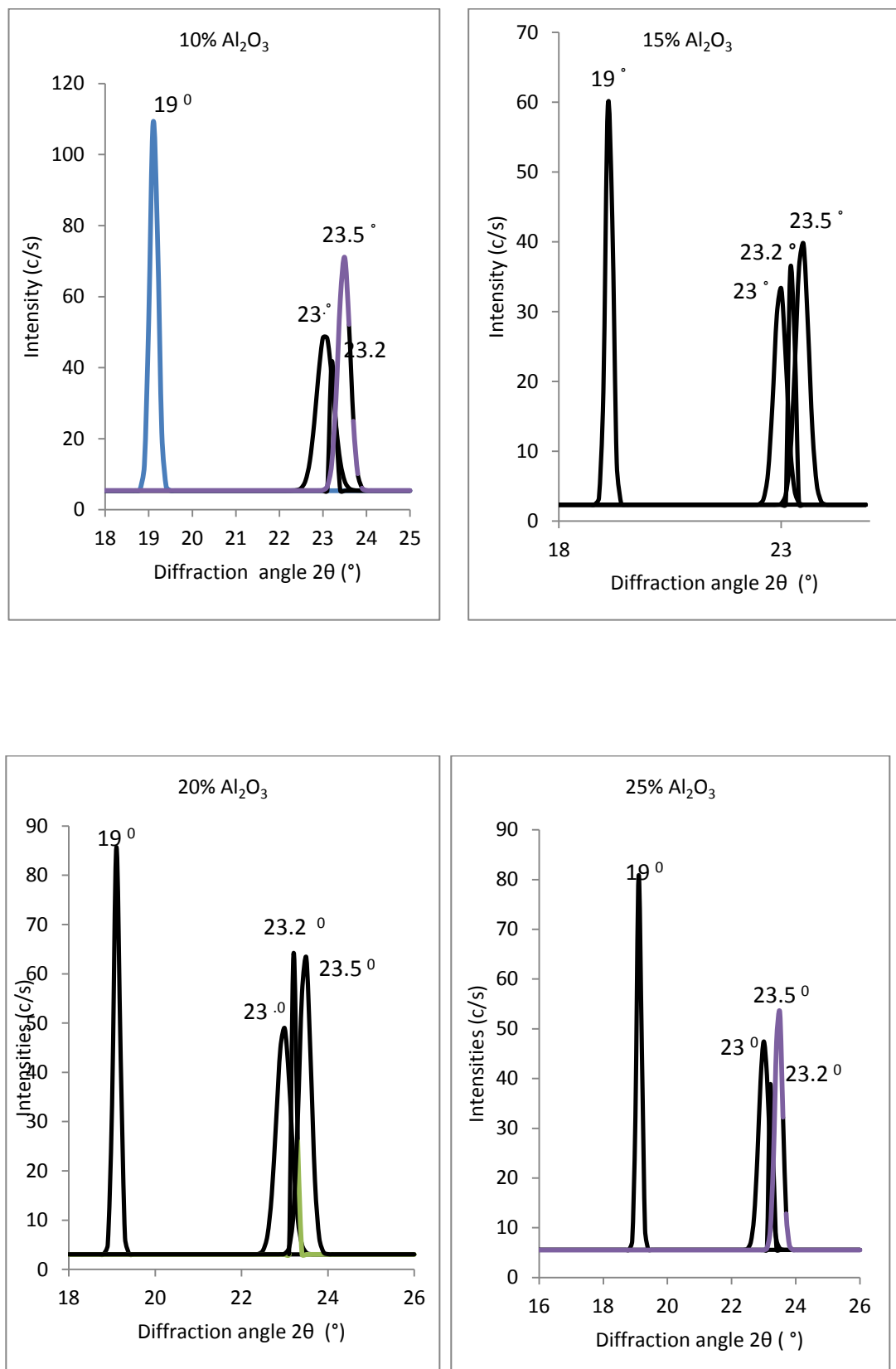


Figure 5.6: Deconvoluted patterns for pure Al_2O_3 and PEO-Li- Al_2O_3 , (5-25 wt %) wt (a) 85.5 wt.%PEO: 9.5wt.% LiI:5 wt.% Al_2O_3 , (b) 81.0 wt.% PEO: 9 wt.%LiI:10 wt.% Al_2O_3 , (c) 76.5 wt.% PEO :8.5 wt.% LiI:15 wt.% Al_2O_3 , (d) 72 .0 wt.%PEO : 8 wt.% LiI:20 wt.% Al_2O_3 , (e) 67.5 wt.% PEO : 7.5 wt.% LiI : 25 wt.% Al_2O_3

Figure 5.7 shows the percentage of crystallinity of polymer electrolyte with different weight percentages of Al_2O_3 . It can be seen that the sample with 15 wt.% Al_2O_3 is more amorphous. It was found for the system added with 15 wt. % Al_2O_3 implying that this system had the least crystalline phase. As we have seen in FTIR, the splitting and broadening of peaks reveals that the incorporation of Al_2O_3 eventually enhances the specific interactions between the surface groups of the ceramic particles and both the PEO segments and the Li salt anions. XRD spectra for 90 wt. % PEO :10 wt. % of LiI sample added with 15 wt.% Al_2O_3 shows that the sample has become more amorphous compared to others and that should exhibit highest ionic conductivity at room temperature. The intensities of the peaks pointing towards the complexation between PEO and salt involving significant suppression of PEO crystalline phase.

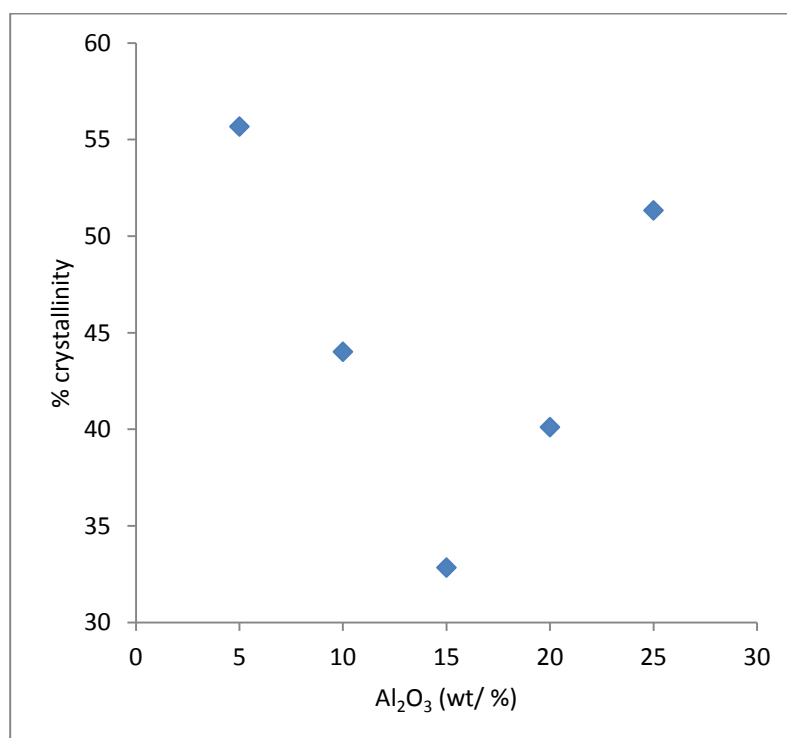
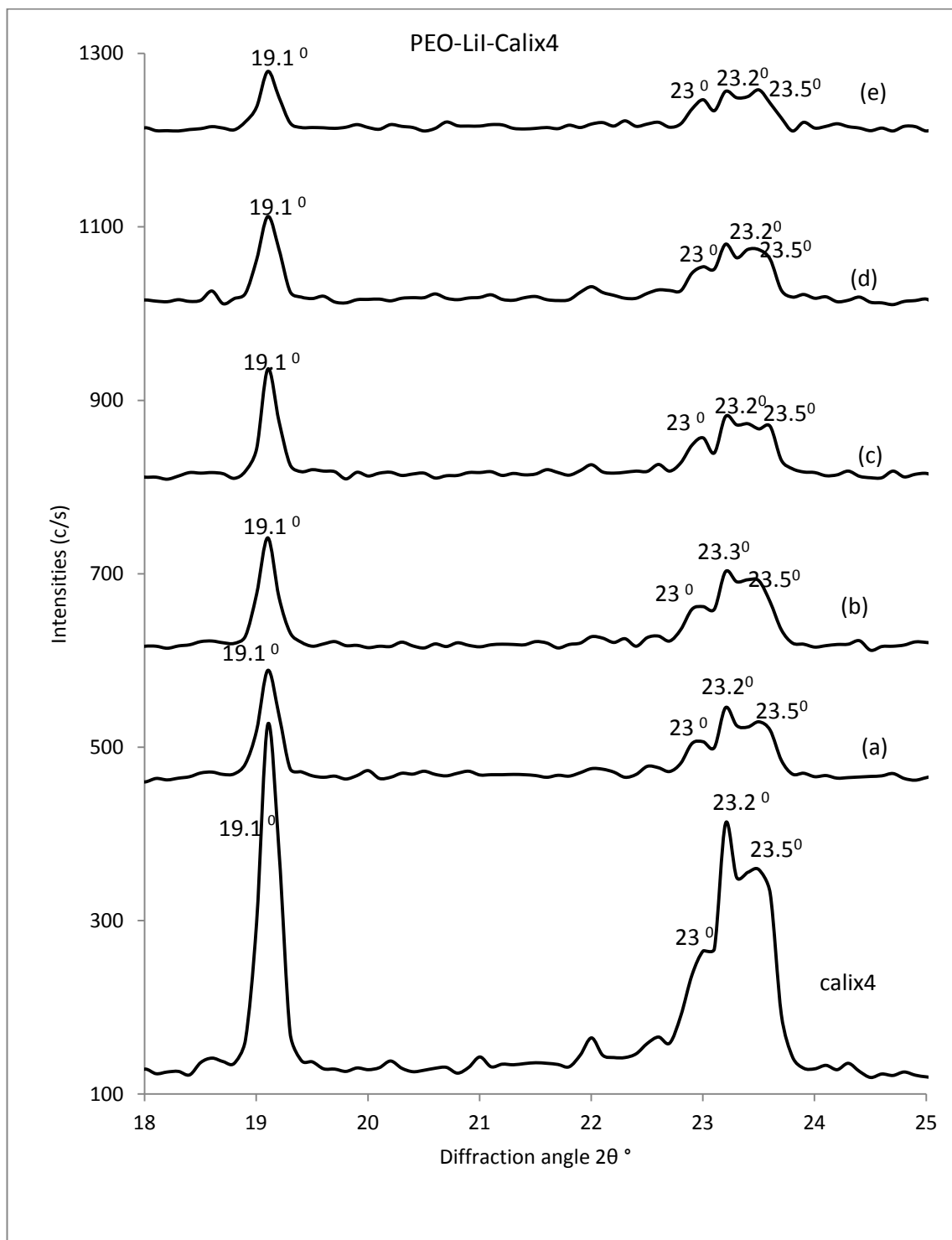


Figure 5.7: Percentage crystallinity of PEO-LiI with different wt. % of Al_2O_3

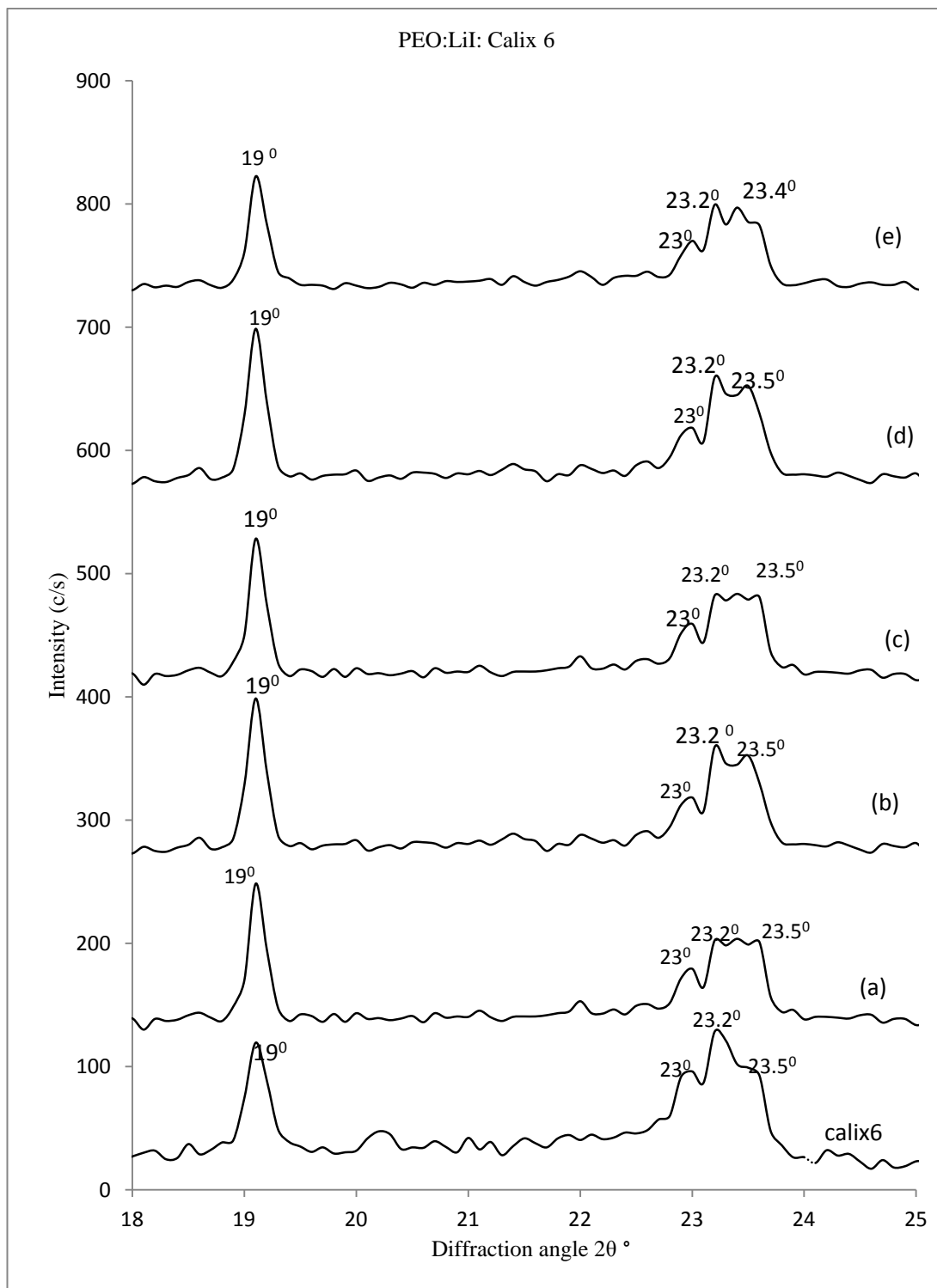
5.4 XRD diffractogram of PEO-LiI system with calix4 and calix6

Figure 5.8 and Figure 5.9 show the XRD patterns obtained for calix4 and calix6 arenes added in different weight percentages to the highest conductivity sample in the PEO-LiI system ie, 90 wt.% PEO:10 wt. % LiI. From the close observation of the peaks at 19° and 23° proves that even high molecular weight polyether somehow interacts with the receptor calix4 and calix6. This can be also attributed to the polymer-calix interactions. The peak near $2\theta = 19^\circ$ is characteristic for the crystalline phase of the pure polymer Kalita et al., (2007). By the increase in weight percentage of the calix arenes the decrease in intensity of the peak at $2\theta = 19^\circ$ shows, there is a decrease in crystallinity of the system. The splitting pattern and the intensity of the peak at $2\theta = 23^\circ$ shows the interactions of calix arenes with polymer salt system.

Figure 5.9 shows the patterns for PEO-LiI-calix6. The less intense peak compared to the pure calix6 shows the more amorphous nature of the system and the complexation. The complexation related to the lithium cation, which is able to interact with oxygen atoms belonging to different polyether chains and the macromolecule receptors. There are no other new peaks observed in this region, shows the absence of any new crystalline complex.

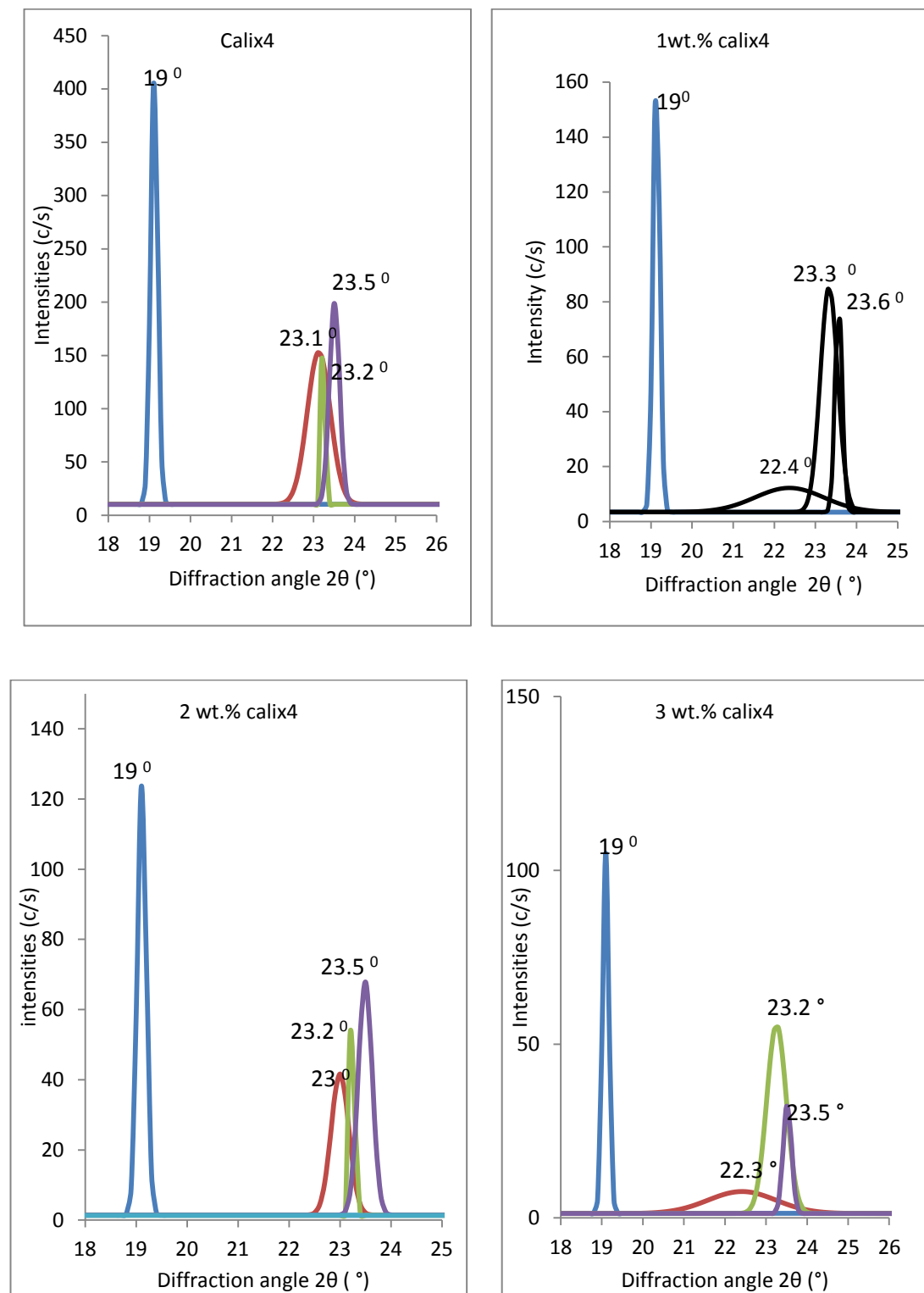


Figure; 5.8: XRD patterns for Calix 4 and PEO:LiI:Calix 4(1-5 wt.%) (a) 89.0wt.% PEO : 10wt.% LiI : 1wt.% Calix 4, (b)88.0wt.% PEO : 10wt.% LiI : 2wt.% Calix 4, (c) 87.0wt.% PEO : 10wt.% LiI : 3wt.% Calix 4, (d) 86.0wt.% PEO : 10wt.% LiI :4 wt.% Calix 4, (e) 85.0wt.% PEO : 10 wt.% LiI : 5 wt.% Calix 4



Figure; 5.9: XRD patterns for Calix6 and PEO:LiI:Calix6 (1-5wt.%) (a) 89.0wt.% PEO : 10wt.% LiI : 1wt.% Calix 6, (b) 88.0wt.% PEO : 10wt.% LiI : 2wt.% Calix 6, (c) 87.0 wt.% PEO : 10wt.% LiI : 3 wt.% Calix 6, (d) 86.0wt.% PEO : 10 wt.% LiI : 4wt.% Calix 6, (e) 85.0wt.% PEO : 10wt.% LiI : 5wt.% Calix 6

Figure 5.10 shows the deconvoluted peaks using Origin software, shows the splitting of peak $2\theta = 23^\circ$ and reduction in intensity of the peak $2\theta = 19^\circ$ compared to pure calix.



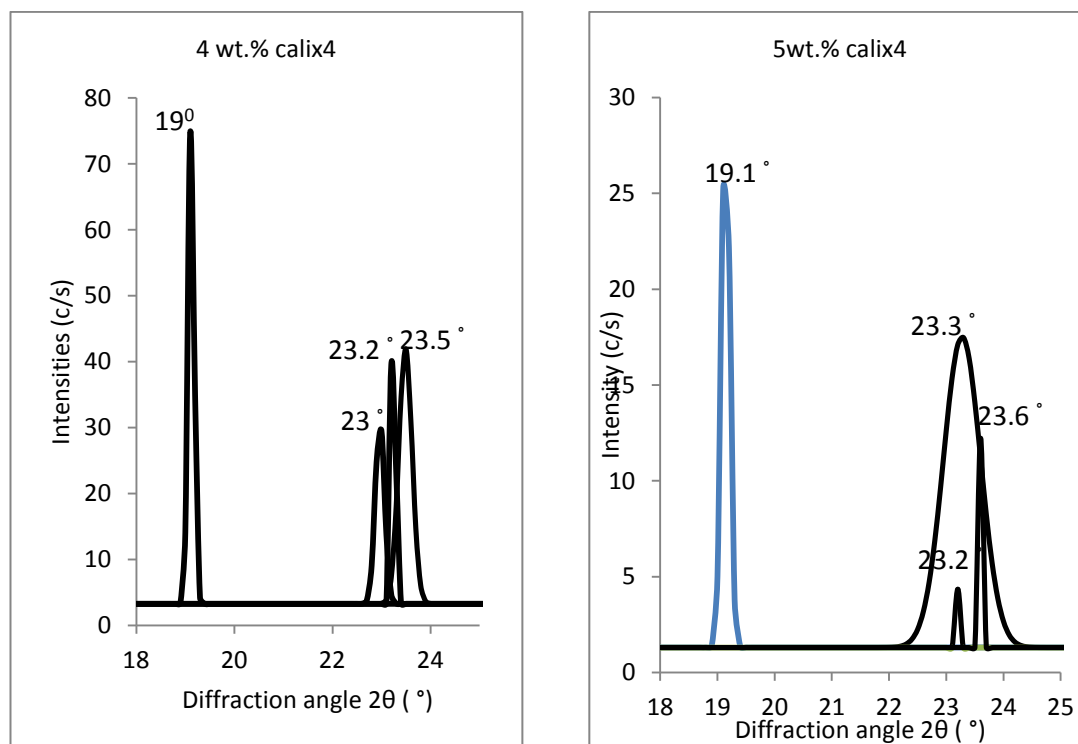
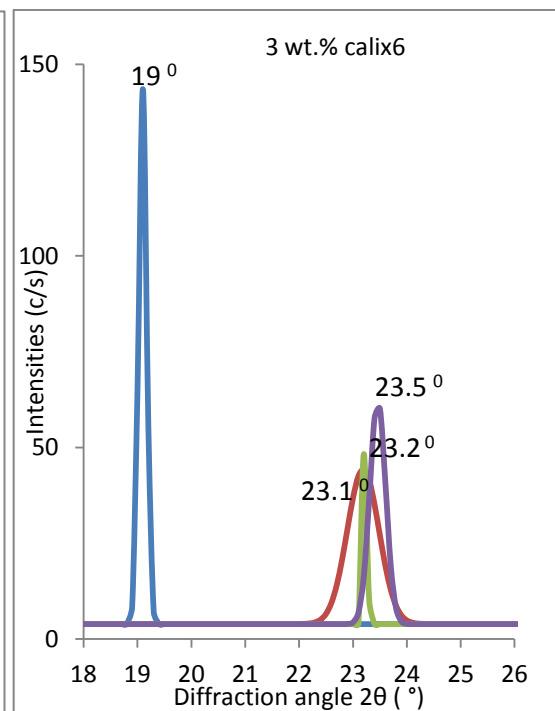
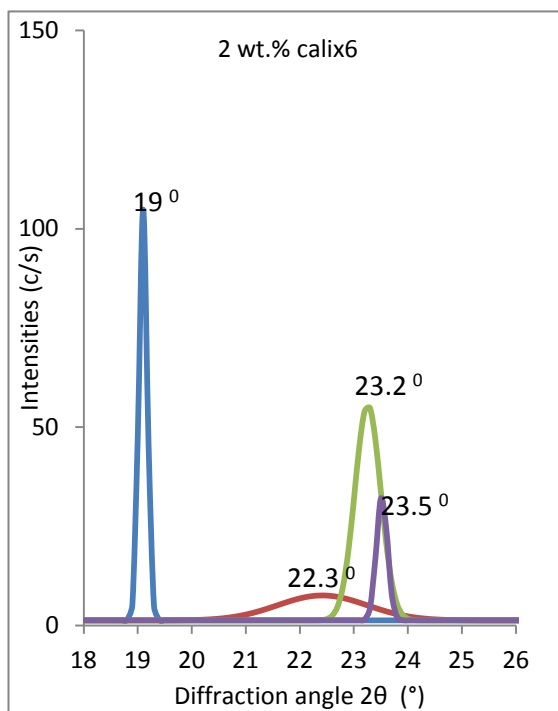
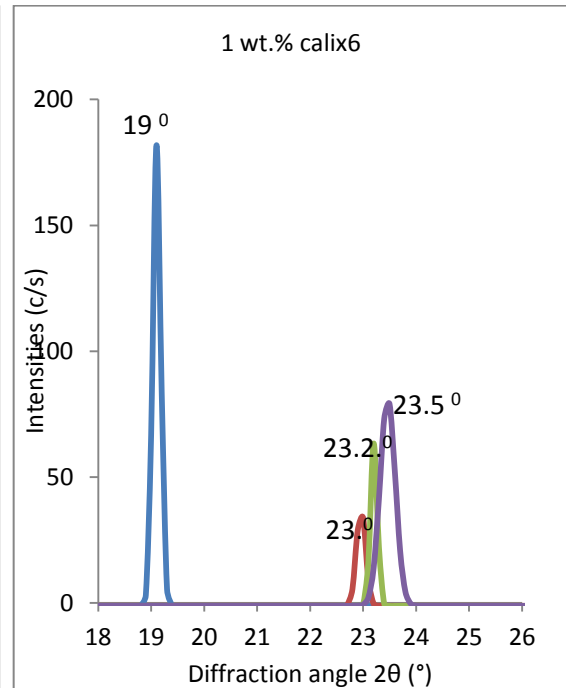
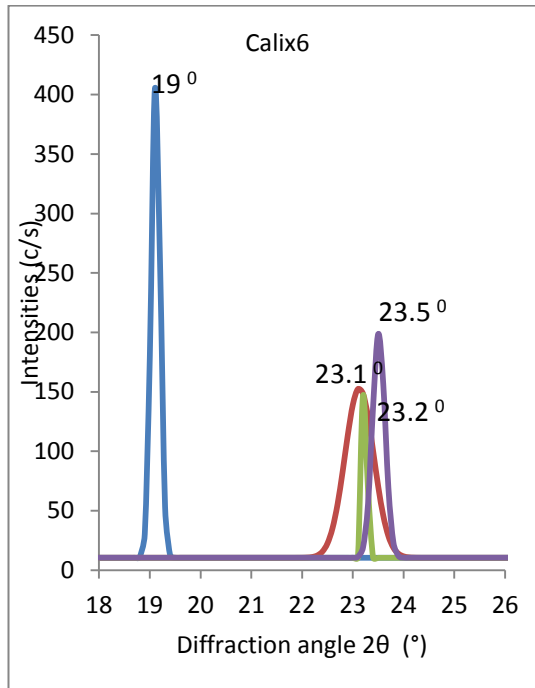


Figure 5.10: Deconvoluted patterns for Calix4 and PEO:LiI:Calix4 (1-5%) (a) 89.0% PEO : 10% LiI : 1% Calix 4, (b)88.0% PEO : 10% LiI : 2% Calix 4, (c) 87.0% PEO : 10% LiI : 3% Calix 4, (d) 86.0% PEO : 10% LiI :4% Calix 4, (e) 85.0% PEO : 10% LiI : 5% Calix 4

Figure 5.11 depicts the splitting patterns of the deconvoluted peak at 23°. The splitting patterns are due to the complexation of salt with the calix6 molecules.



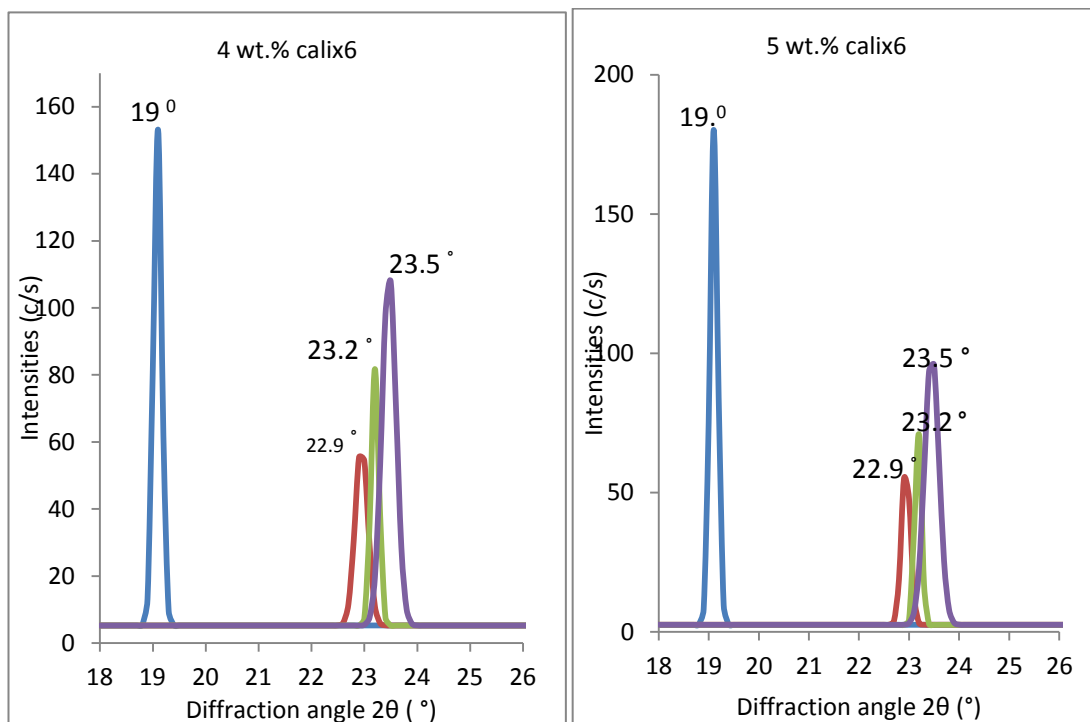


Figure 5.11: Deconvoluted patterns for Calix6 and PEO:LiI:Calix6 (1-5 wt.%) (a) 89.0wt.% PEO : 10 wt.% LiI : 1wt.% Calix6, (b)88.0wt.% PEO : 10wt.% LiI : 2wt.% Calix 6, (c) 87.0wt.% PEO : 10wt.% LiI : 3wt.% Calix 6, (d) 86.0wt.% PEO : 10wt.% LiI :4wt.% Calix 6, (e) 85.0wt.% PEO : 10wt.% LiI : 5 wt.% Calix6.

Figure 5.12 depicts the variation in percentage crystallinity of calix4 and calix6 content in PEO salt complexes measured using Origin software. The least crystallinity was found for system added with 3wt.% calix4 and system with 3 wt.% calix6, since being the most amorphous. The XRD patterns show that the formation of a less crystalline salt-PEO complex by the addition of Calix4 and Calix6 arenes. It shows a better compatibility between supramolecular receptor and the PEO polymer matrix which agrees with the FTIR results.

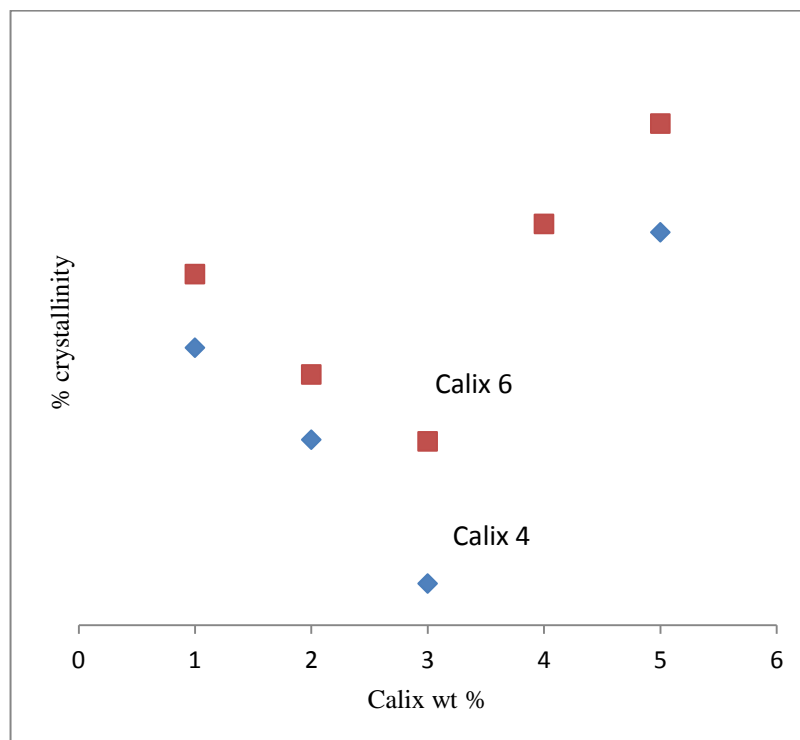


Figure 5.12: Percentage crystallinity of Calix4 and Calix6, 1-5 wt. %

5.5 Summary

From X-Ray diffractogram of pure samples and samples with the addition of receptors decreases the crystallinity. But the effect is more pronounced with increase in percentage of inorganic and organic receptors which is consistent with the FTIR data. The role of inorganic filler is not limited to sole action of preventing crystallization of the polymer chains but also, and in particular, of promoting specific interactions between surface groups and both the PEO segments and the electrolyte ionic species that we have discussed in this chapter and the previous chapter.