CHAPTER 5

RESULTS ON
MORPHOLOGY AND STRUCTURAL STUDIES OF POLY(ε-CAPROLACTONE) COMPLEXES

5.1 Introduction

Many polymers are semi-crystalline, containing both crystalline and amorphous phases. Polymer chains that are arranged in regular order are crystalline. In between crystalline regions, polymer chains are randomly entangled forming a disorganized state and these represent the amorphous phase. Thus, crystallinity refers to the degree of structural order in the polymer matrix.

Chain folded model of the crystallites has been accepted since 1950s. The polymer chains folded back and forth upon themselves so that adjacent segments were parallel to give the crystal structure called lamella. A semi-crystalline polymer film may show the circular shape spherulite morphology. The development of a spherulite starts from an individual crystal nucleus, radiate out with arrays of lamella like the spokes of a bicycle wheel. In between lamella, there are amorphous regions as shown in Fig. 5.1.

Surface morphology studies were carried out using Scanning Electron Microscopy (SEM). SEM can give an insight on the shape, size, texture and/or phase distribution of the solid polymer electrolyte system. Often, a rough surface is correlated to the higher degree of crystallinity while the addition of plasticizers demonstrates a smoother topology with less phase separation.

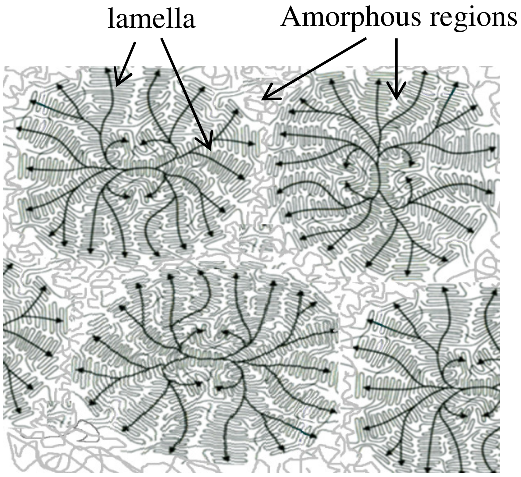
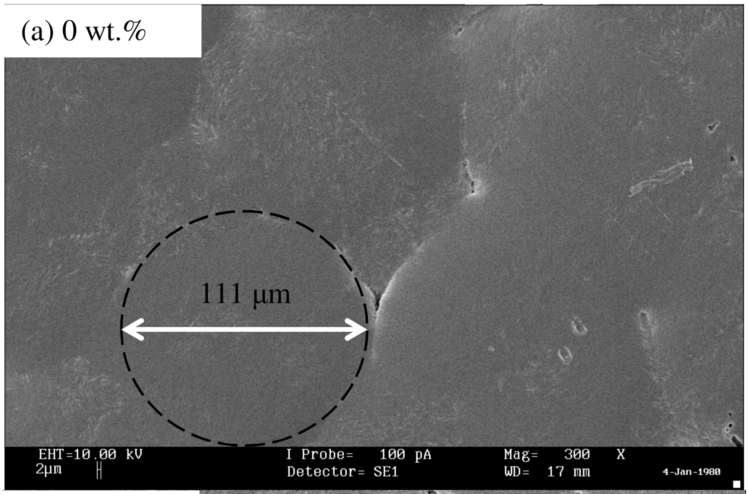


Fig. 5.1 Schematic diagram of spherulite morphology.

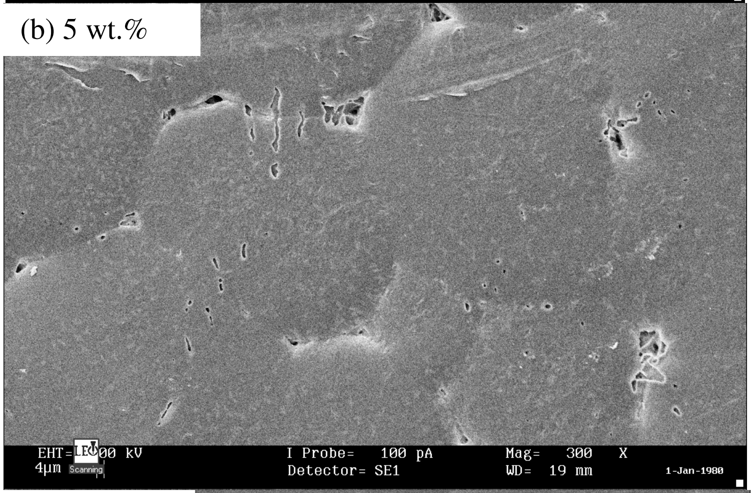
Even though Gadjourova *et al.*, (2001) has demonstrated that crystalline complexes of PEO_6:$LiXF_6$ (X = P, As, Sb) exhibit ionic conductivity, the values are still low. Many researchers have reported that amorphous polymers often showed higher ionic mobility and conductivity. The degree of crystallinity is another important factor that can greatly affect the physical and chemical behavior of any polymer electrolyte system. In the present work, XRD is used to determine the degree of crystallinity of the polymer membrane.

5.2 Morphology studies of PCL-NH_4SCN system

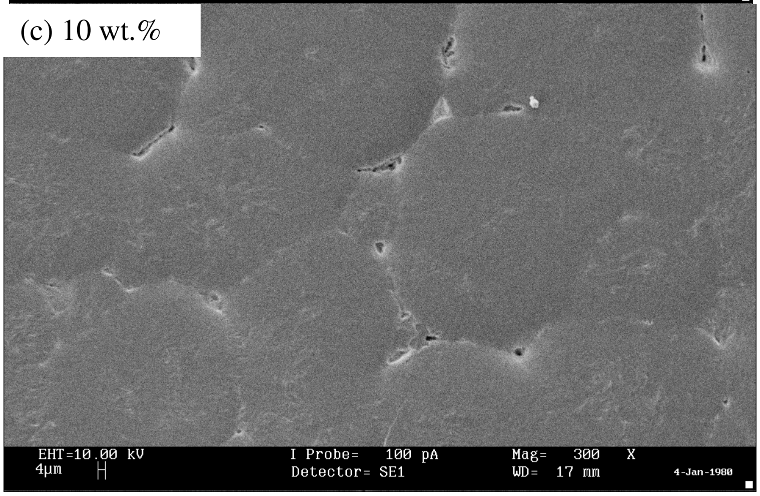
The samples were coated with a thin layer of gold to prevent electrostatic charging. Fig. 5.2 shows the 300 times magnified SEM micrographs of PCL-NH_4SCN samples added with 0 to 32 wt.% NH_4SCN. The average diameter of spherulites from micrograph of PCL-NH_4SCN films is plotted as a function of salt concentration in Fig. 5.3.



(a) 0 wt.%

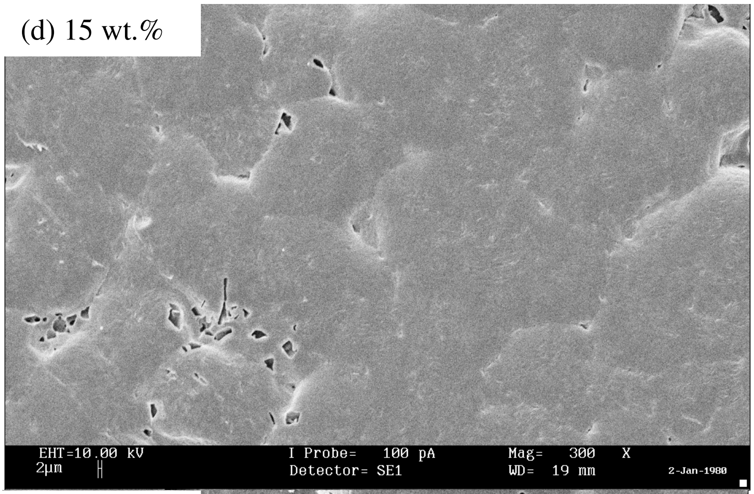


(b) 5 wt.%

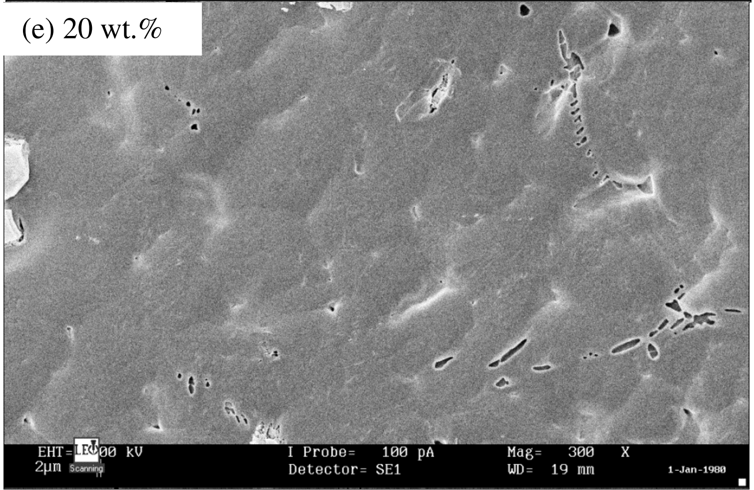


(c) 10 wt.%

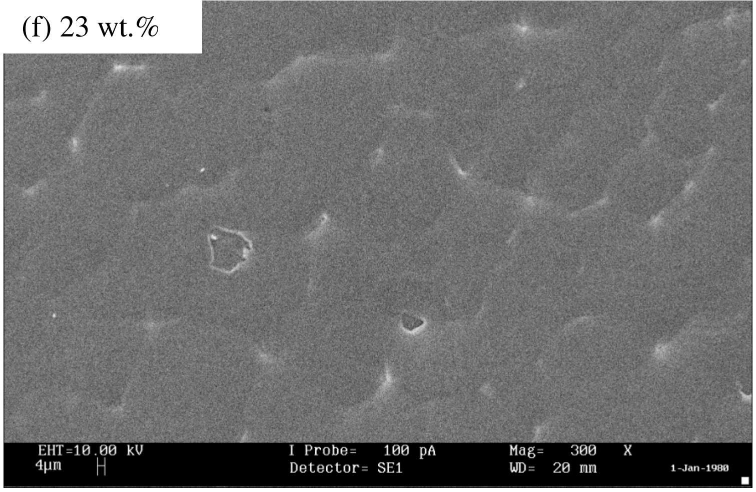
(d) 15 wt.%



(e) 20 wt.%



(f) 23 wt.%



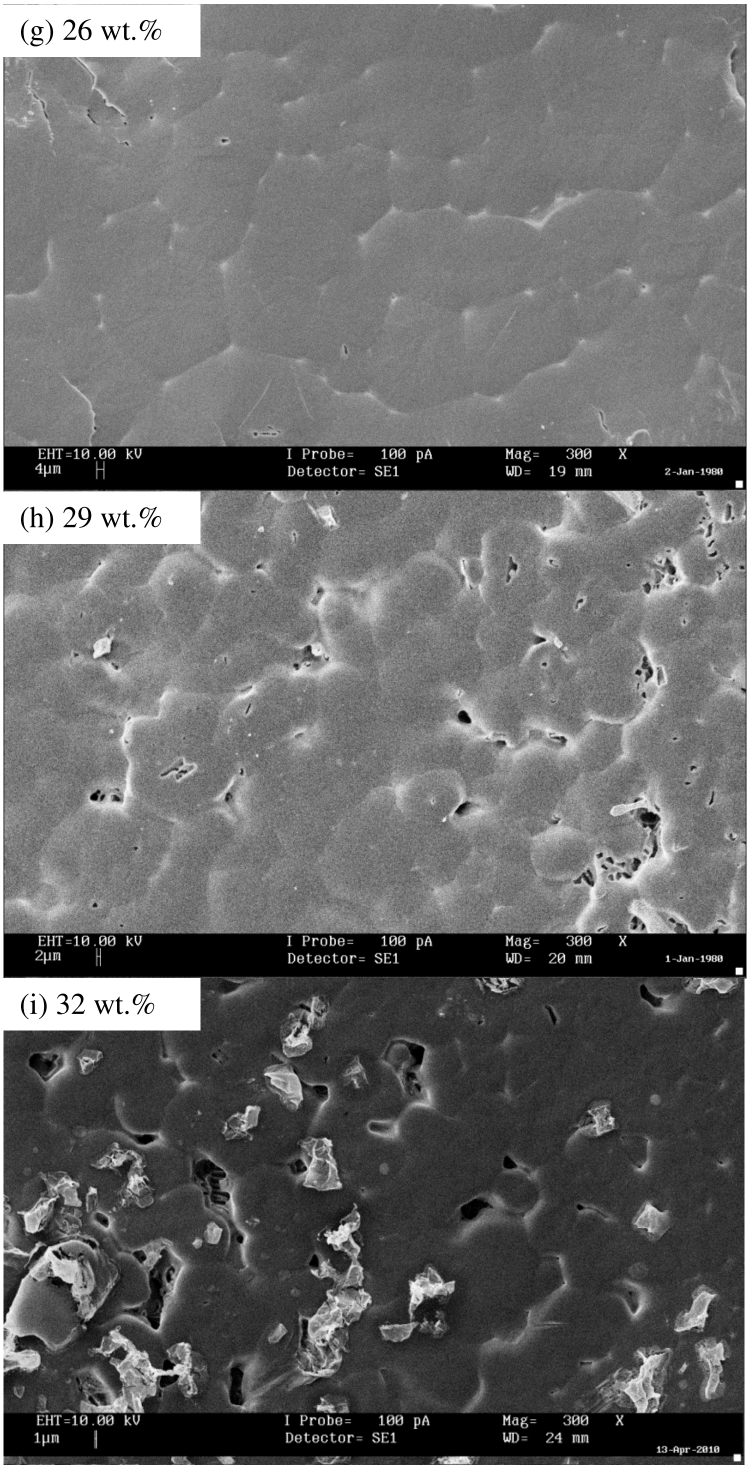


Fig. 5.2 Micrographs (300x) of PCL-NH_4SCN films added with 0 to 32 wt.% NH_4SCN at room temperature.

Spherulitic morphology is clearly observed for pure PCL film as shown in Fig. 5.2(a). These circular-shape spherulites of different sizes are the result from uniform radial lamella growth in which lamella is made up of folded chains. Parts of the amorphous phase is also observed. Amorphous phase is defined as the intra-crystalline phase that exists as micro domains embedded between the spherulites [Sreekanth *et al.*, 1999].

The average size of the spherulites is measured to be approximately 111 μm in diameter or ~12300 μm^2 in area. The boundaries are also clear after impingement with the adjacent spherulites. Such morphology has been reported by [Pereira *et al.*, 2009] in polymer blends based on PEO and starch.

When 5 wt.% of NH_4SCN is added to PCL film, more crystalline domains with smaller size are observed. This also means an increase of the micro domain amorphous fraction. The surface morphology is a little rough but no clear phase separation is observed in Fig. 5.2(b). This indicates an excellent distribution of ammonium salt in PCL matrix. As more salt is incorporated to PCL-NH_4SCN films, from 10 wt.% up to 26 wt.% as shown in Fig. 5.2 (c) to (g) respectively, the number of spherulites continue to increase tremendously and their size become much smaller.

The average diameter of these spherulites is depicted in Fig. 5.3. It is observed to drop with increasing salt content. Similar decreasing of spherulite size was observed by Reddy and Chu (2002) in PEO-KI system and Sreekanth *et al.* (1999) in PEO-$NaNO_3$ system.

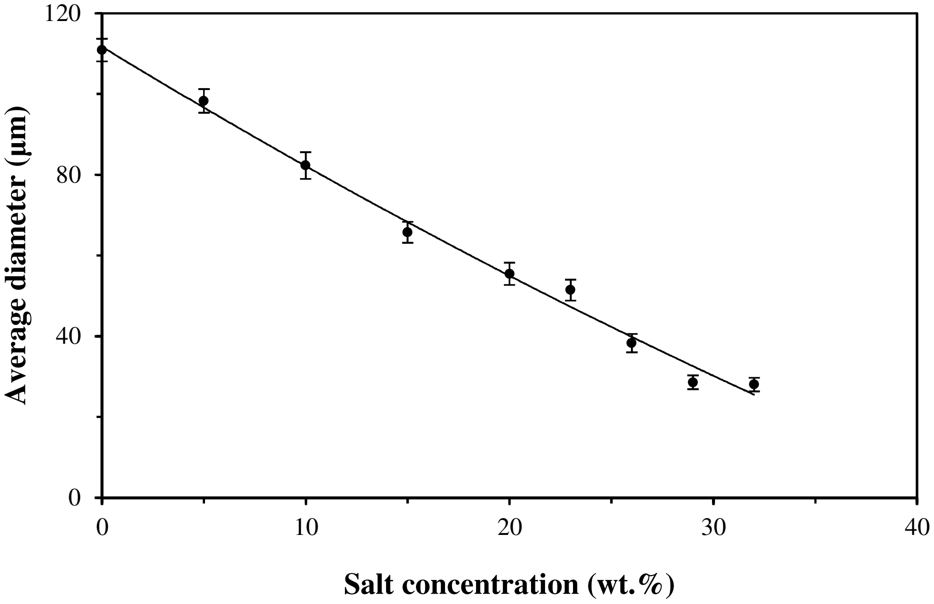
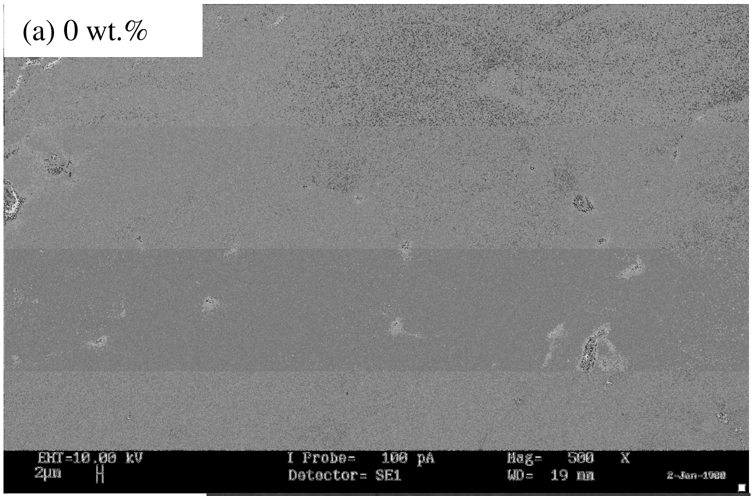


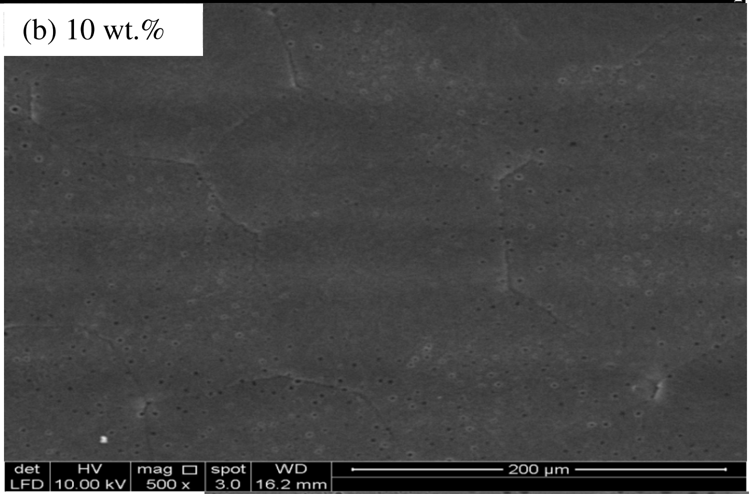
Fig. 5.3 Salt concentration dependence of average diameter of spherulites from micrograph of PCL-NH_4SCN films.

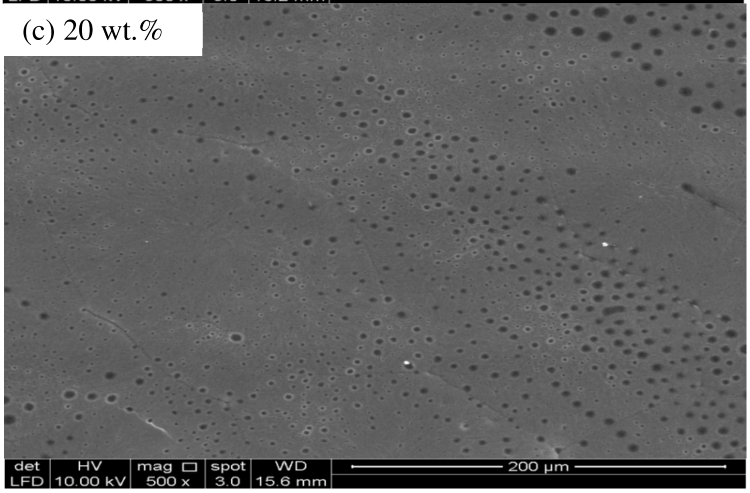
At 29 wt.% salt content, the spherulite size and roughness remain the same but agglomeration appears and more so in sample containing 32 wt.% salt, as shown in Fig. 5.2(h) & (i), respectively. This is attributed to the excess salt ions that cause formation of ion clusters or higher aggregates. It is noticed that PCL-NH_4SCN complexes rich in NH_4SCN are more brittle.

5.3 Morphology Studies of PCL-NH_4SCN-EC system

Fig. 5.4 shows the 500 times magnified SEM micrographs of samples at various EC concentrations in wt.%.


(a) 0 wt.%


(b) 10 wt.%


(c) 20 wt.%

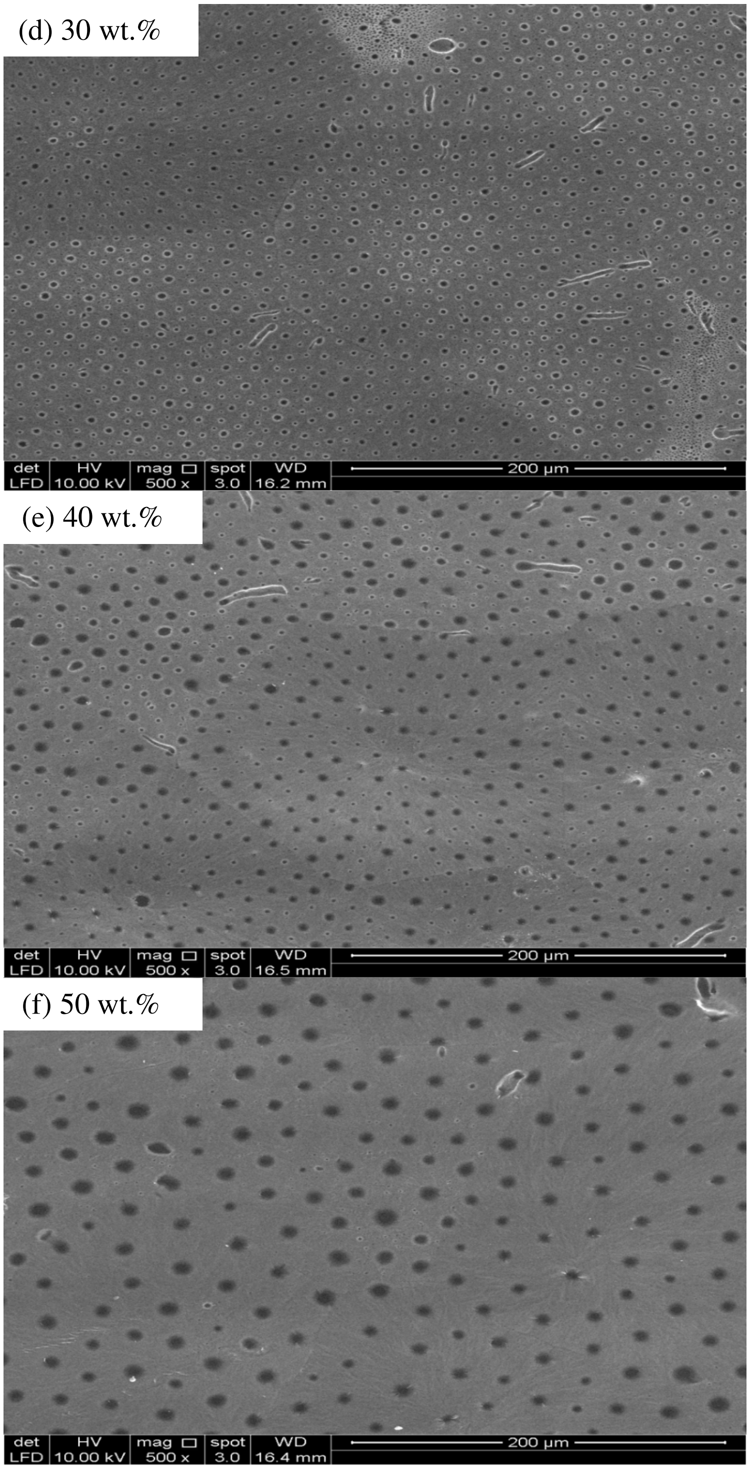


Fig. 5.4 Micrographs (500x) of PCL-NH_4SCN-EC films added with 0 to 50 wt.% EC at room temperature.

Dramatic changes of surface morphology are presented with incorporation of EC as plasticizer. When 10 wt.% of EC was added to PCL-NH_4SCN (74:26) matrix, SEM examination in Fig. 5.4 (b) reveals that generally the size of spherulites retains but the boundaries are not as definite as 0 wt.% EC in Fig. 5.4 (a). At the same time, new pore-like phases are observed to start appearing on the surface though not prominent. The samples are softer and less brittle.

With increasing plasticizer content to 20 wt.%, more noticeable pore-like phases is observed and these visible new phases become well distributed at 30 wt.%, as shown in Fig. 5.4(d). The spherulite border becomes less defined. Referring back to section 4.3, DSC results of this PCL-NH_4SCN-EC system shows new crystalline melting peak that decreases with increasing EC content. Therefore, the new pore-like morphology observed on the surface could be possibly due to new PCL-EC crystalline complex phases.

At 40 wt.% of EC content, the spherulite boundaries are fading away and the surface appears to be smoother, as can be seen in Fig. 5.4(e). Finally, Fig.5.4(f) shows a borderless smooth surface with addition 50 wt.% of EC. This soft film with smooth surface is closely associated with the presence of EC. The clear spherulite boundaries is no longer been observed showing a huge interruption of the crystalline phase with addition of new pore-like phases. It is therefore anticipated that the 50 wt.% EC sample has the least degree of crystallinity which will be analyzed in the XRD studies in the following section.

5.4 X-Ray Diffraction of PCL-NH_4SCN system

Fig. 5.5 presents the XRD pattern of pure PCL membrane without ammonium salt.

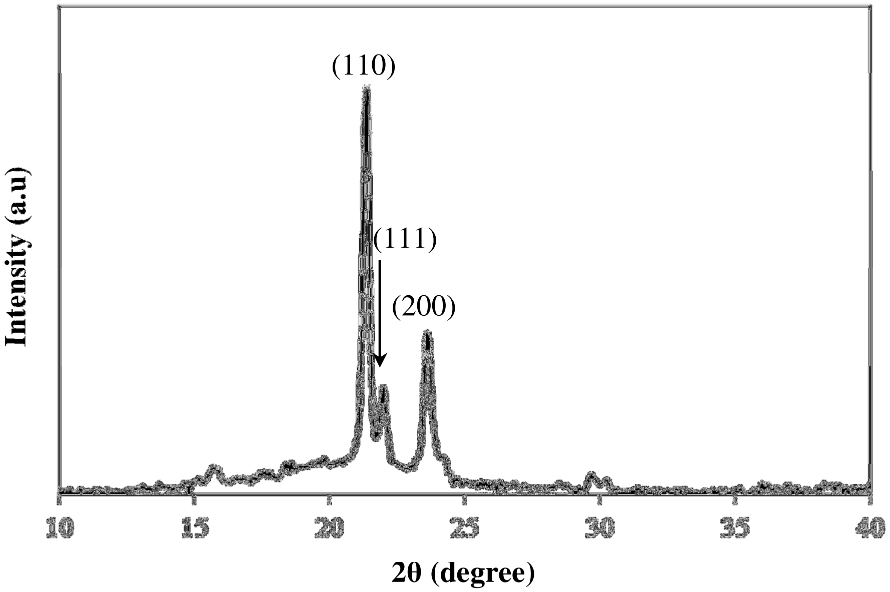


Fig. 5.5 XRD pattern of pure PCL membrane without ammonium salt.

Three strong diffraction peaks were clearly observed in Fig. 5.5 at Bragg 2θ = 21.4°, 22.0° and 23.7° corresponding to the (110), (111) and (200) orientations, respectively, of the orthorhombic crystal structure [Chen and Wu, 2007]. An amorphous halo centered around 2θ = 21.0° is also observed. This indicates that the semi-crystalline PCL film is composed of both crystalline and amorphous phases.

Fig. 5.6 contains the XRD pattern of pure NH_4SCN salt and PCL:NH_4SCN complexes with various weight ratios. As can be seen from Fig. 5.6, the intensities of the PCL dominant peaks decrease with increasing salt concentration up to 26 wt.%. This indicates a decrease in degree of crystallinity, χ_C . At 29 wt.% and 32 wt.% salt, reflections of the presence of free salt are clearly seen. In order to calculate the degree of crystallinity, the overlapping PCL spectrums were deconvoluted to separate the crystalline peak from amorphous spectrum, as illustrated in Fig. 5.7.

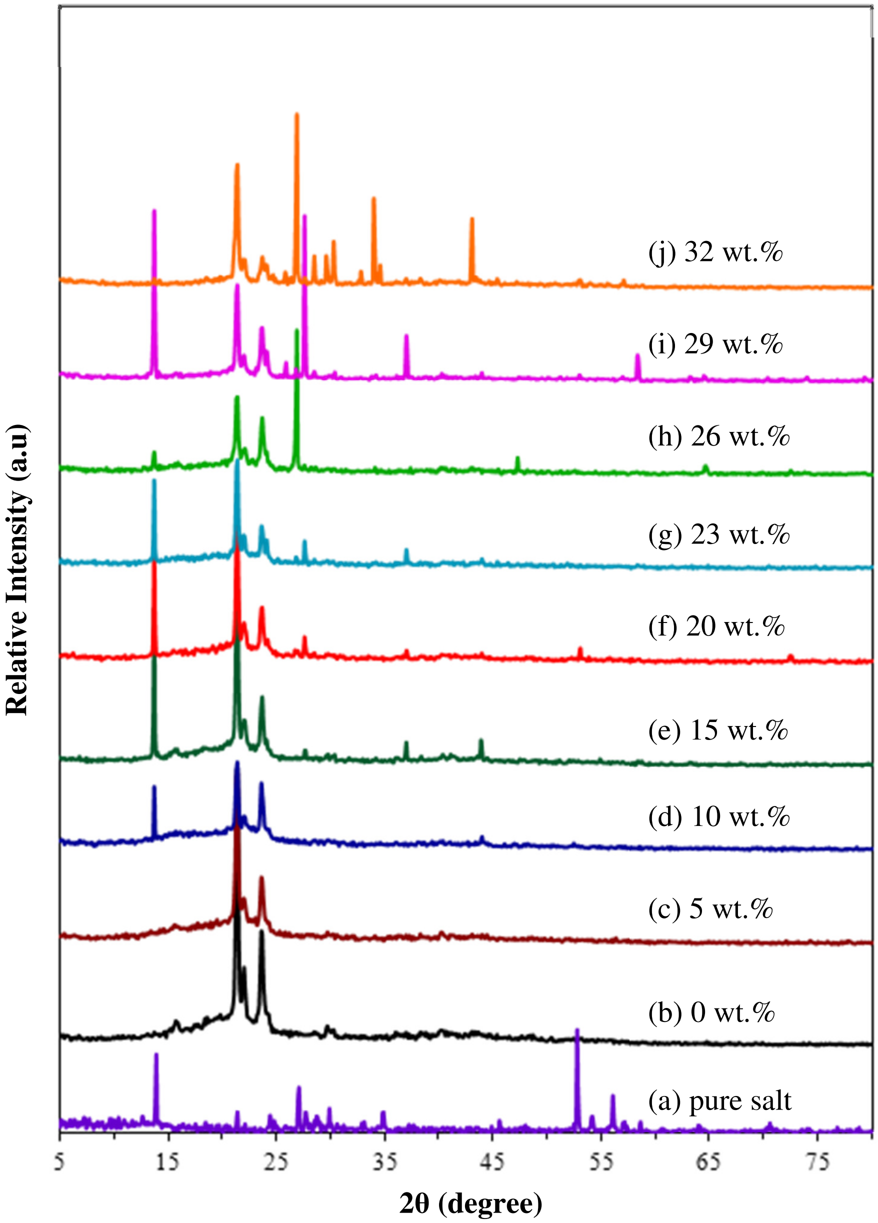
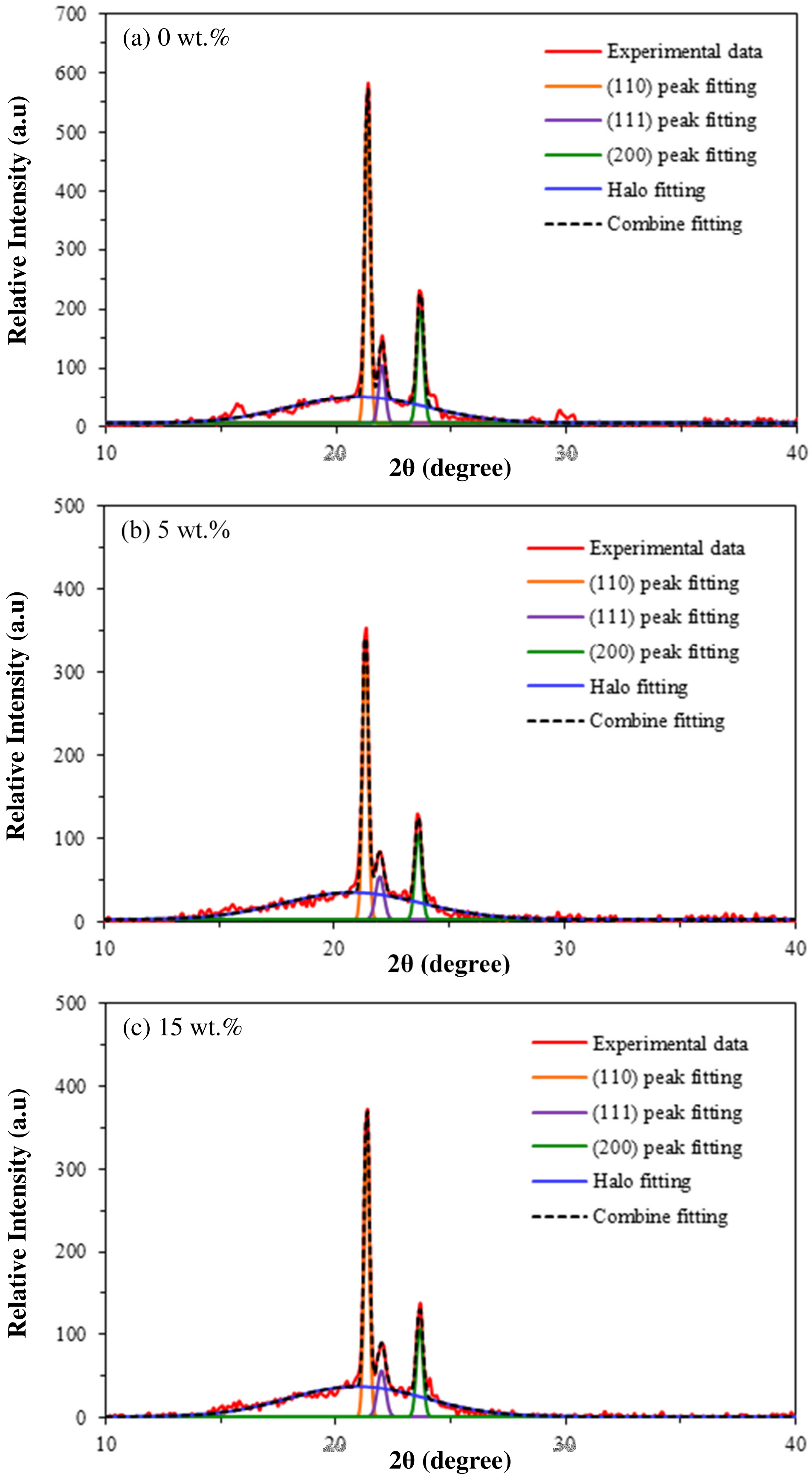
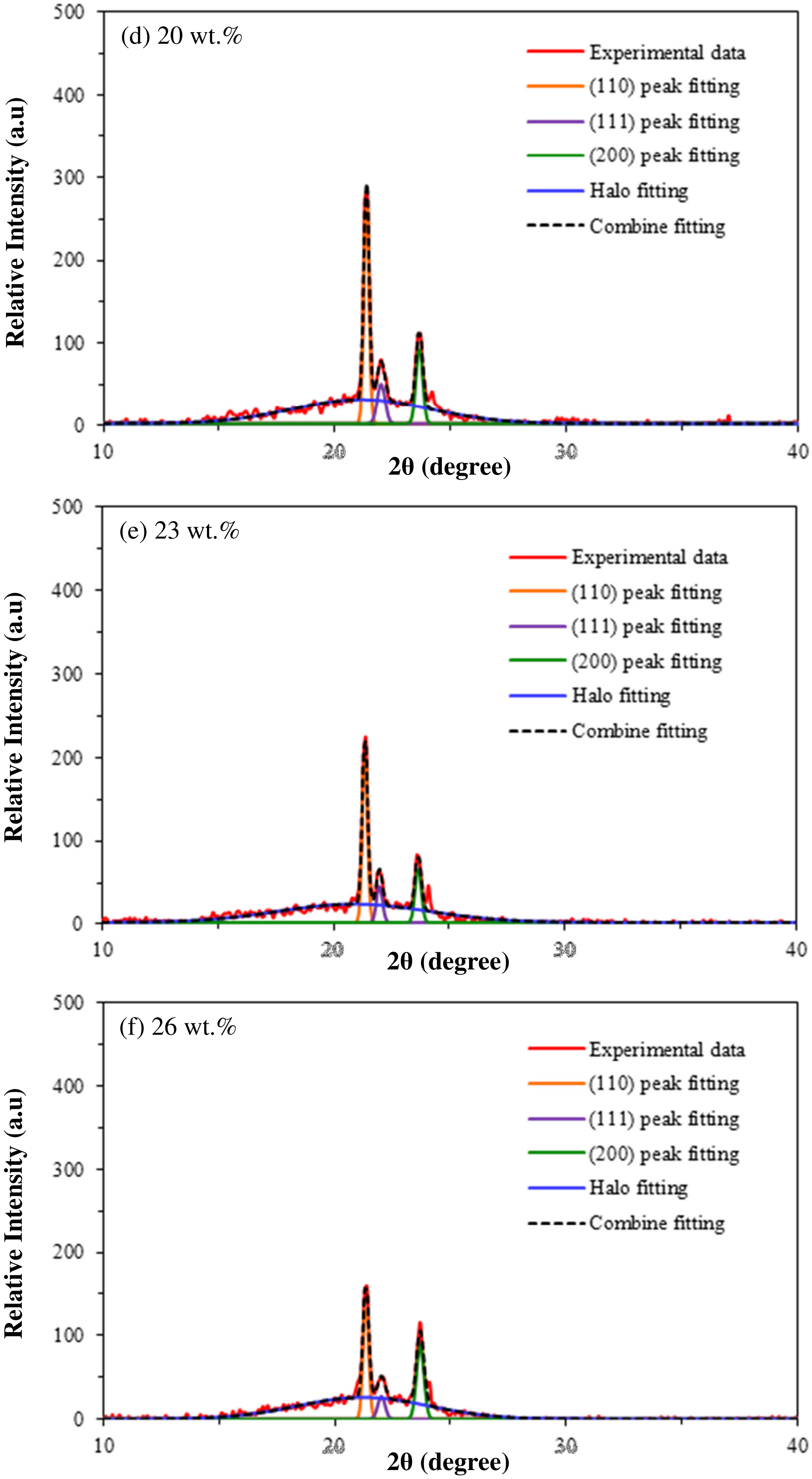


Fig. 5.6 XRD patterns of (a) pure NH_4SCN salt and PCL-NH_4SCN films added with 0 to 32 wt.% NH_4SCN at room temperature.


(a) 0 wt.%
(b) 5 wt.%
(c) 15 wt.%
Relative Intensity (a.u)
2θ (degree)
0
100
200
300
400
500
600
700
10
20
30
40
Experimental data
(110) peak fitting
(111) peak fitting
(200) peak fitting
Halo fitting
Combine fitting


(d) 20 wt.%
Experimental data
(110) peak fitting
(111) peak fitting
(200) peak fitting
Halo fitting
Combine fitting
Relative Intensity (a.u)
500
400
300
200
100
0
10
20
30
40
2θ (degree)
(e) 23 wt.%
Experimental data
(110) peak fitting
(111) peak fitting
(200) peak fitting
Halo fitting
Combine fitting
Relative Intensity (a.u)
500
400
300
200
100
0
10
20
30
40
2θ (degree)
(f) 26 wt.%
Experimental data
(110) peak fitting
(111) peak fitting
(200) peak fitting
Halo fitting
Combine fitting
Relative Intensity (a.u)
500
400
300
200
100
0
10
20
30
40
2θ (degree)

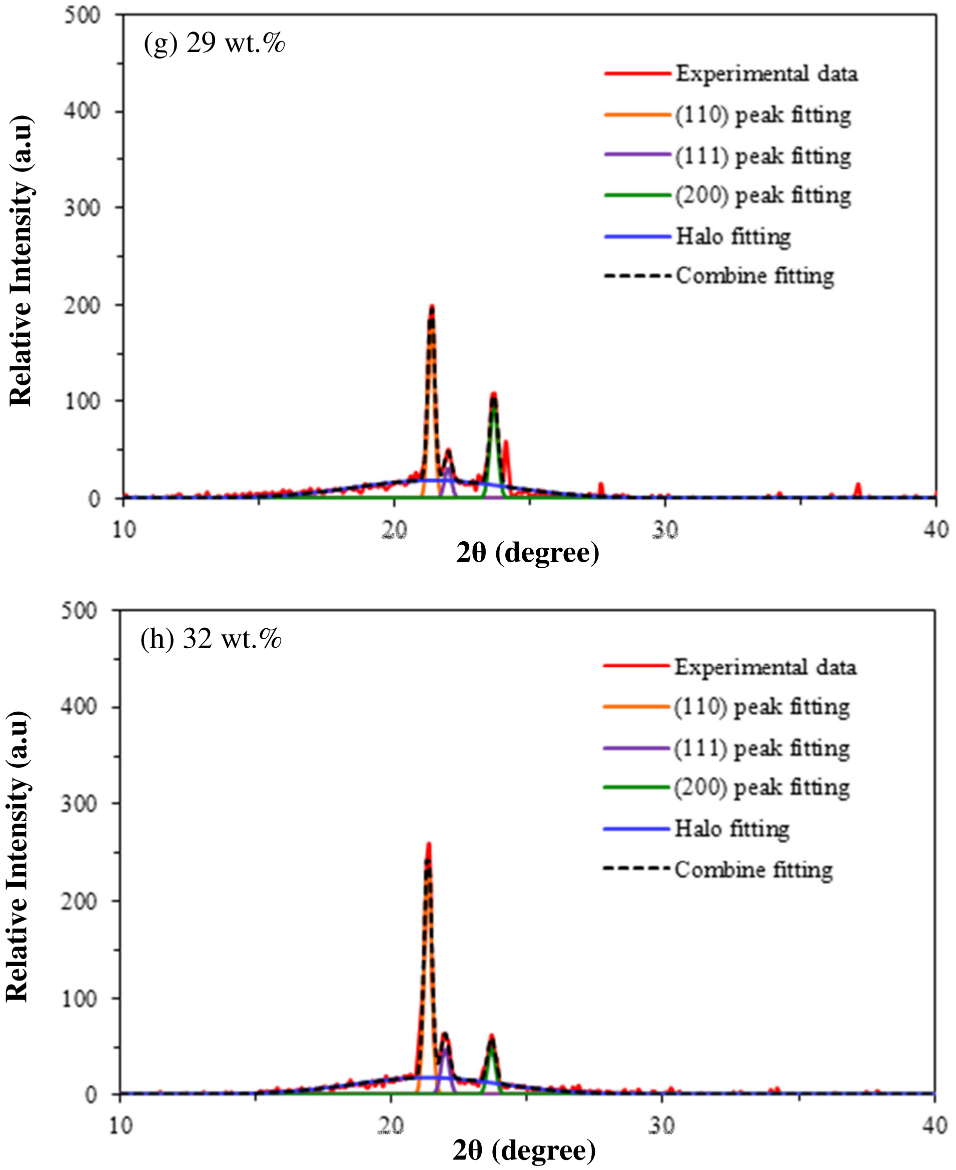


Fig. 5.7 The curve fitting XRD patterns of PCL-NH_4SCN films added with 0 to 32 wt.% NH_4SCN.

The relative degree of crystallinity as a function of salt concentration is then plotted in Fig. 5.8. It is calculated from the respective integrated area, according to equation 3.3.

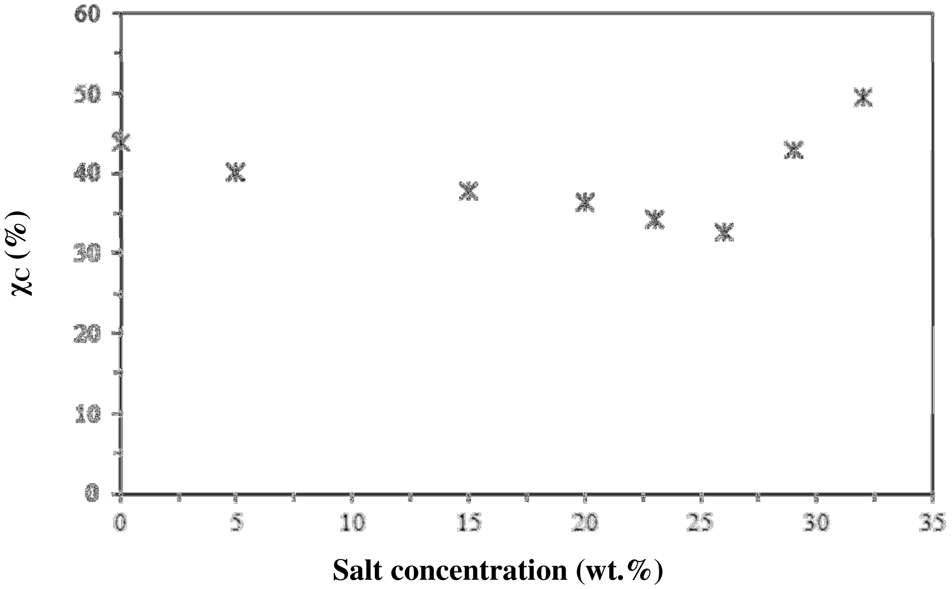


Fig. 5.8 Relative degree of crystallinity as a function of salt concentration, calculated from XRD pattern.

The relative degree of crystallinity, χ_C of pure PCL is estimated to be 43.8 %. This value is similar as compared to XRD result being carried out by Wang and co-workers (2008) who obtained 45.3 % for pure PCL microspheres. χ_C is found to decrease gradually to 40.2 % and 37.7 % at 5 wt.% and 15 wt.% salt, respectively. χ_C continues to drop to 36.3 % and 34.3 % until a minimum value of 32.7 % upon adding 26 wt.% of salt into the polymer complex.

The degree of crystallinity is found to increase at 29 wt.% onwards and is correlated to re-association of mobile ions. These surfactants (free ions) would form micelles (ion clusters) after a threshold salt concentration as reported by Teeters *et al.* (1996).

This decreasing trend of χ_C up to 26 wt.% calculated structurally is in good agreement with that obtained thermally from chapter 4. Thus, the reduction in the degree of crystallinity can be correlated to the formation of complexation between PCL and ammonium ions as discussed in previous chapter. As more salt is accommodated into the PCL crystalline phase, it depresses the crystalline phase of PCL. If this result is true then the ionic conductivity variation will be a mirror image of Fig. 5.8 with a peak at 26 wt.%.

5.5 X-Ray Diffraction of PCL-NH_4SCN-EC system

One of the major drawbacks of the polymer-salt system is the limitation of ionic conductivity at room temperature. Various methods were proposed and investigated to improve the conductivity. It was reported that conductivity predominates in the amorphous phase [Berthier *et al*., 1983] as proven by NMR studies. The introduction of plasticizer would reduce the glass transition temperature of the complex, suppress crystallinity and improve the salt dissociation capability.

In the current work, ethylene carbonate (EC) is added as plasticizer to the least crystalline sample in the PCL-NH_4SCN system. Fig. 5.9 displays the XRD pattern of (a) pure NH_4SCN, (b) pure PCL and PCL-NH_4SCN-EC films added with 0 to 50 wt.% EC.

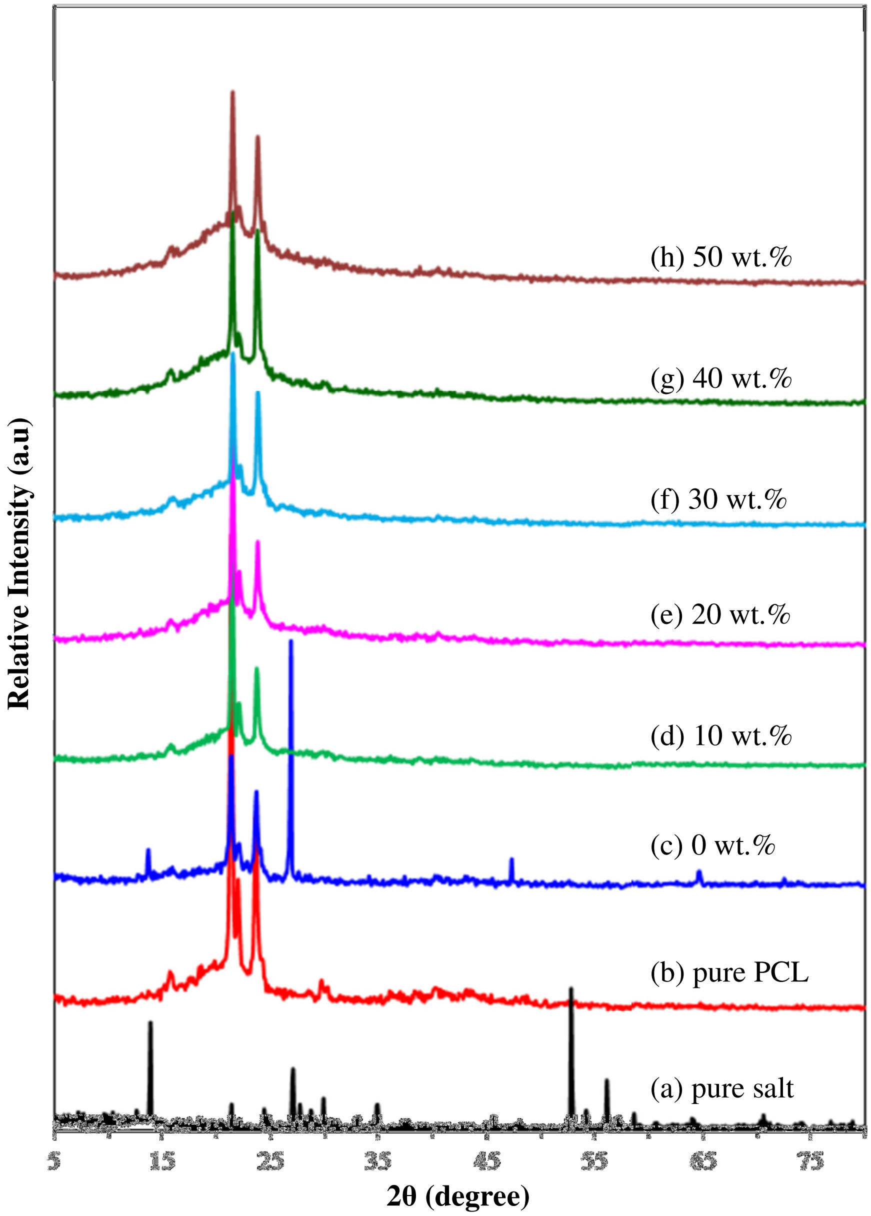
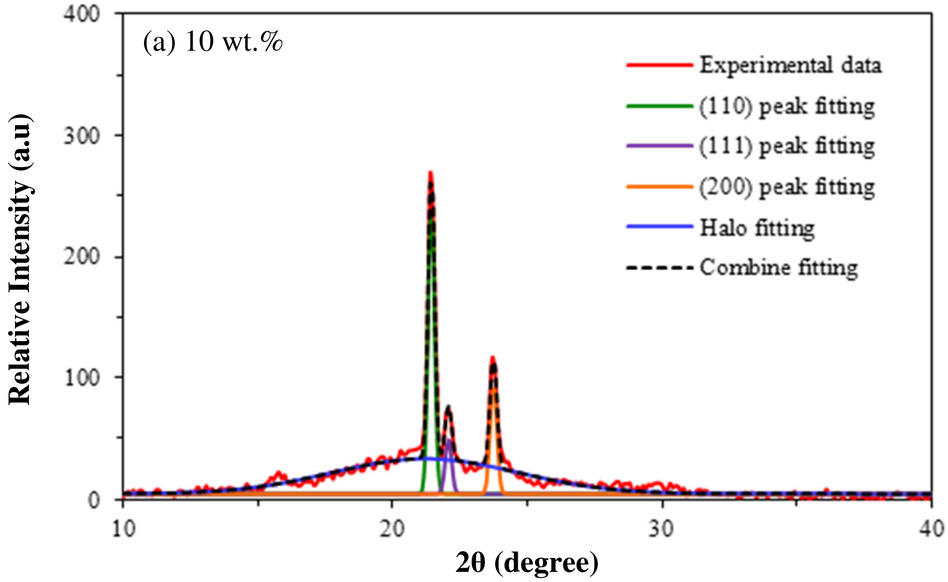
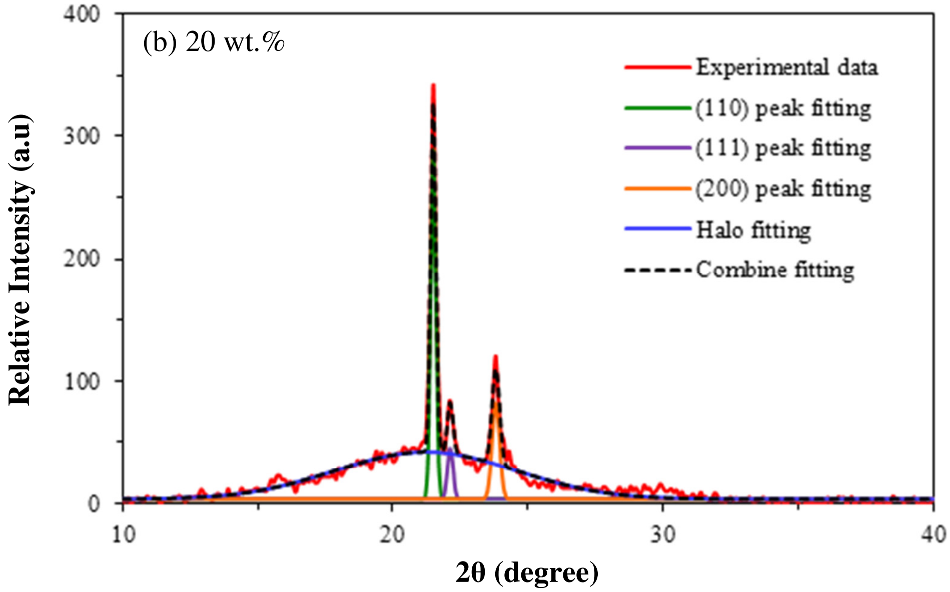


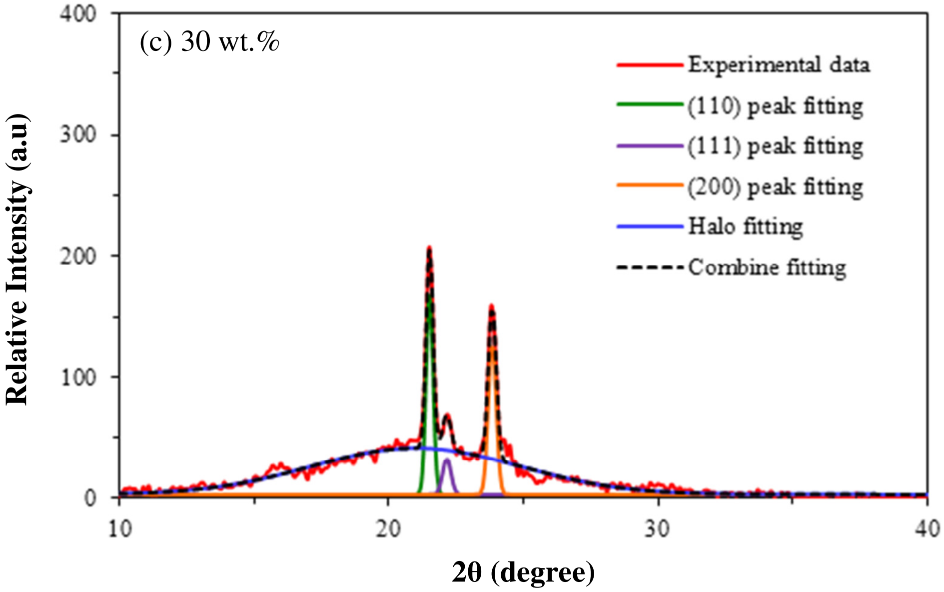
Fig. 5.9 XRD patterns of (a) pure NH_4SCN, (b) pure PCL and PCL-NH_4SCN-EC films added with 0 to 50 wt.% EC at room temperature.

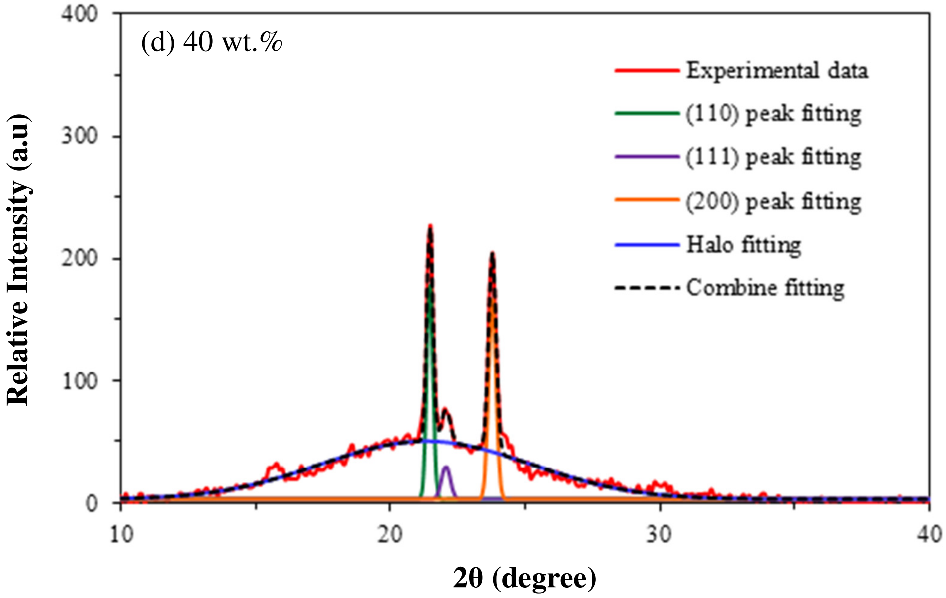
It can be seen from Fig. 5.9 that addition of EC to the PCL-NH_4SCN generates significant disorder into the polymer structure with higher amorphousness. Although the crystalline peaks remain sharp and strong in intensities, the amorphous spectrum generally has become stronger and broader with increasing EC content.

In order to calculate the relative degree of crystallinity, PCL crystalline peaks were separated from the amorphous spectrum with high goodness of fit as depicted in Fig. 5.10 (a)-(e).






(c) 30 wt.%
Experimental data
(110) peak fitting
(111) peak fitting
(200) peak fitting
Halo fitting
Combine fitting
Relative Intensity (a.u)
0
100
200
300
400
10
20
30
40
2θ (degree)


(d) 40 wt.%
Experimental data
(110) peak fitting
(111) peak fitting
(200) peak fitting
Halo fitting
Combine fitting
Relative Intensity (a.u)
0
100
200
300
400
10
20
30
40
2θ (degree)

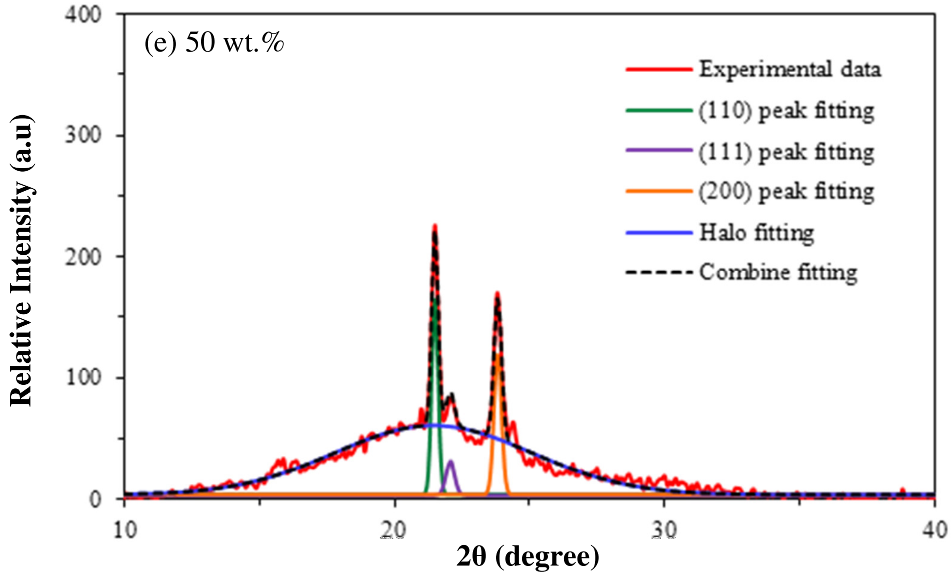


Fig. 5.10 The curve fitting XRD patterns of PCL-NH_4SCN-EC films added with 0 to 50 wt.% EC.

The relative degree of crystallinity as a function of EC concentration is then calculated from the respective integrated area and is shown in Fig. 5.11.

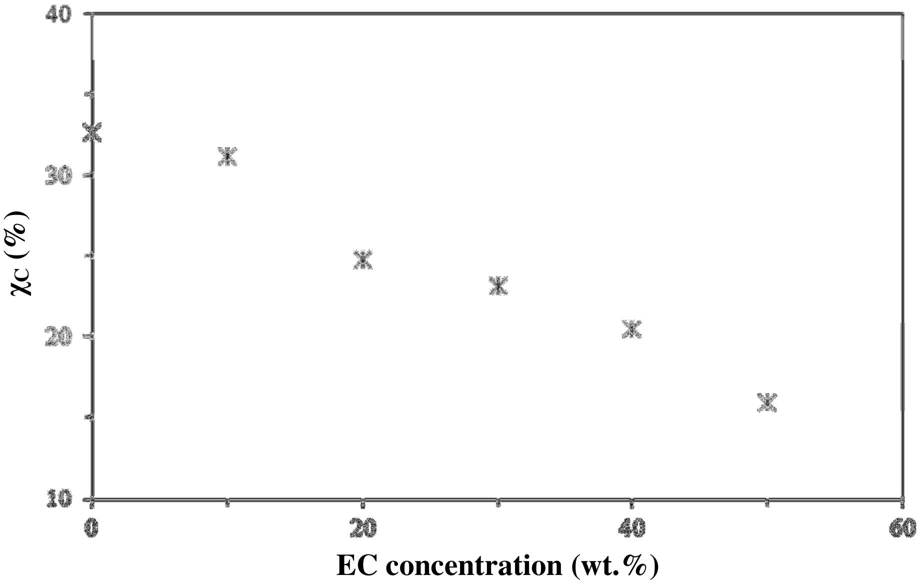


Fig. 5.11 Relative degree of crystallinity as a function of EC concentration, calculated from XRD pattern.

The degree of crystallinity, χ_C is found to decrease slightly from 32.7 % to 31.2 % upon addition of 10 wt.% EC. χ_C of the ternary system is observed to drop continuously to 24.8 %, 23.1 %, 20.5 % and 16.0 % with addition of 20 wt.%, 30 wt.%, 40 wt.% and 50 wt.% EC, respectively. The drop of χ_C is consistent with other EC plasticized systems reported in [Jiang *et al.*, 1997; Bandara *et al.*, 1998]. EC has disrupted the crystalline phase of the polymer matrix and therefore reducing the degree of crystallinity. This observation is consistent with thermal studies in previous chapter.

5.6 Summary

In morphology studies:

- For PCL-NH_4SCN system, round-shape spherulites with definite boundaries are observed. When more NH_4SCN is added up to 26 wt.%, the number of spherulites increase massively with corresponding reduction in spherulite size. The surface morphology become less rough and no clear phase separation is observed. Addition of 29 wt.% salt and beyond shows the appearance of agglomeration due to the formation of ion clusters.

- For PCL-NH_4SCN-EC system, incorporation of EC causes dramatic changes of surface morphology. The clear spherulite boundaries are no longer observed and the surface becomes smooth. New pore-like phases that could be attributed to new PCL-EC crystalline complex phases appear. EC seems to disrupt a large portion of the crystalline phase and produce a soft film with smooth surface.

In structural studies:

- For PCL-NH_4SCN system, the intensities of the PCL crystalline peaks decrease with increasing NH_4SCN concentration. The degree of crystallinity is found to decrease gradually from 43.8 % of pure PCL film to a minimum 32.7 % at 26 wt.% salt.

- For PCL-NH_4SCN-EC system, the amorphous spectrum has become stronger and broader with increasing EC content as can be seen clearly after deconvolution in Fig. 5.10. χ_C drops continuously from 32.7 % to 16.0 % upon addition of 0 wt.% and 50 wt.% of EC, respectively. EC has disrupted the crystalline phase, reducing the degree of crystallinity of the polymer matrix. This observation is consistent with thermal studies in the previous chapter.

How can the reduction in degree of crystallinity be understood from ion-polymer, polymer-plasticizer, ion-plasticizer interactions? This will be dealt in FTIR analysis in Chapter 6.