4.1 Introduction

In this chapter different techniques were used to characterize solid polymer electrolytes (CS:AgTf, CS:LiTf and CS:NaTf) and nano-composite polymer electrolytes ((1-x)(0.9CS:0.1AgTf)-xAl₂O₃ (0.02 ≤ x ≤ 0.1), (1-x)(0.9CS:0.1NaTf)-xAl₂O₃ (0.02 ≤ x ≤ 0.1) and (1-x)(0.9CS:0.1LiTf)-xAl₂O₃ (0.02 ≤ x ≤ 0.1)). Structural and morphological techniques are important to characterize solid and nanocomposite polymer electrolytes. X-ray diffraction is the most powerful method to investigate the effect of inorganic salts and fillers on structural property of polymers. Scanning electron microscopy (SEM) is a currently used method to investigate the surface morphology of polymer electrolytes and nanocomposite electrolytes. In combination with SEM, EDX was used to further analyse the surface morphology of the samples. In this work UV-vis and TEM were also used to characterize silver nanoparticles formed as a result of silver ion reduction in the CS:AgTf system.
4.2 Structural and morphological analysis of SPEs based on CS:AgTf

4.2.1 XRD analysis of SPE based on CS:AgTf

In the present study, XRD was used to reveal the nature of the complexed film whether amorphous or crystalline. X-ray diffraction is a powerful tool for investigating the crystallinity and structural changes in a polymer electrolyte membrane [Seo et al., 2009]. Figure 4.1 shows several crystalline peaks at around 8.2°, 16.3°, 22.2°, 23.7°, 40.8°, and 47.5° for pure silver triflate. This is in good agreement with the diffractogram of pure silver triflate as reported in the literature [Kim et al., 2006].

![Figure 4.1 XRD pattern of pure AgCF₃SO₃.](image)

Figure 4.2 (a-f) depicts the XRD pattern of pure chitosan and CS:AgTf complexes. It is observed that the two peaks in the diffractogram of pure chitosan disappear and a broad halo is observed which indicates occurrence of complexation between the silver salt and chitosan. The crystalline peaks of pure AgTf is absent in the electrolyte membrane.
However, the small peak appeared at $2\theta = 38^\circ$, in all chitosan-silver triflate complexes may be attributable to silver particle formation because this peak cannot be observed in pure chitosan. This phenomenon may be more understood in the case of XRD study at different temperatures. Moreover another peak at $2\theta > 10^\circ$ is also observed in the sample designated as CSA3.

![X-ray diffractogram](image)

Figure 4.2 X-ray diffractogram of (a) CSA1 (pure chitosan), (b) CSA2, (c) CSA3, (d) CSA4, (e) CSA5 and (f) CSA6.

To further study the crystalline structure of the samples Origin 8 software has been used to obtain the full width at half maximum (FWHM). From the FWHM the crystallite size of the samples can be calculated by using the Debye–Scherrer formula and to observe whether the crystalline region is increased or decreased upon the addition of the salt or inorganic filler [Ramesh et al., 2011, Aravindan et al., 2009]. Crystallite size measurement is an important method to detect the amorphous domain because the peak
broadening (large FWHM) of the polymer is directly related to the increased amorphous contribution [Sunkyu et al., 2010]. Figure 4.3 (a-c) reveals the results of gaussian fitting on pure chitosan (CSA1), CSA3 (4 wt.% of AgTf) and CSA6 (10 wt.% of AgTf) samples. It can be seen that the pure chitosan sample have crystalline peaks at 10.5°, 15.1°, 17.7° and 20.9° which is not obvious in Figure 4.2 (a). According to literature [Pawlicka et al., 2008, Belamie et al., 1999, Osorio-Madrazo et al., 2011], these crystalline peaks (10.5°, 15.1°, 17.7° and 20.9°) of pure chitosan can be ascribed to the reflection planes of (020), (110), (220) and (200). Deconvolution of the diffractogram for sample CSA3 reveals that the crystalline peak at 10.5° shifts to 11.5°, the crystalline peak at 17.7° shifts to 18.3° and the main crystalline peak of pure chitosan at 20.9° shifts to 23.1° for CS:AgTf (CSA3) sample. A sharp crystalline peak at 38.1° is attributable to silver nanoparticle. The gaussian fitting on CSA6 sample shows one broad halo which indicates the increase of the amorphous domain of the sample. To study the amorphousness of the samples the coherent length (crystallite size) was calculated using the following relation,

\[
L = \frac{0.9\lambda}{\Delta2\theta_b \cos \theta_b}
\]  

(4.1)

where \(\lambda\) is X-ray wavelength, \(\Delta2\theta_b\) is full width at half maximum (FWHM) and \(\theta_b\) is the peak location. The large FWHM value (Table 4.1) for CSA6 sample indicates the amorphousness of CSA6 sample compared to CSA1 (pure chitosan) and CSA3 sample. The calculated crystallite size (Table 4.1) reveals that with increasing salt concentration the amorphous domain increased. In principle, coherent length defines the crystallite size of polymer electrolytes. Based on Debye–Scherrer equation, the broader the diffraction peak width, the shorter is the crystallite size. Samples with smaller crystallite
size exhibits higher ionic conductivity [Ramesh et al., 2011]. Thus the decrease in intensity and broadening of the peaks indicate the increase in amorphous domain as a result of disruption of the crystalline phase of the chitosan by the AgTf salt. The degree of crystallinity for the selected SPEs based on chitosan was calculated using Equation 4.2,

\[
(\chi) \% = \frac{A_C}{(A_A + A_C)} \times 100
\]

(4.2)

where \(A_C\) and \(A_A\) are the total area of crystalline and amorphous regions respectively. It is interesting to note that the degree of crystallinity is suppressed more effectively upon the addition of more AgTf salt which can be ascribed to the disruption of the polymer crystalline phase [Reddy and Chu, 2002]. At a high salt content (10 wt.\%) the system is completely amorphous as no chitosan crystalline peak can be observed.
Figure 4.3 Gaussian fitting of XRD for (a) CSA1 (pure chitosan), (b) CSA3 and (c) CSA6 samples.

Table 4.1, $2\theta$, FWHM, crystallite size (L) and degree of crystallinity ($\chi$) for selected CS:AgTf SPE samples.

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>$2\theta$ (degree)</th>
<th>FWHM (rad)</th>
<th>L (Å)</th>
<th>Degree of Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSA1</td>
<td>20.6</td>
<td>0.083733</td>
<td>17</td>
<td>18.7</td>
</tr>
<tr>
<td>CSA3</td>
<td>22.8</td>
<td>0.095944</td>
<td>15</td>
<td>15.3</td>
</tr>
<tr>
<td>CSA6</td>
<td>19.7</td>
<td>0.132578</td>
<td>11</td>
<td>-</td>
</tr>
</tbody>
</table>
Moreover, the X-ray diffraction patterns at different temperatures demonstrate some crystalline peaks which can be attributed to silver nanoparticles within the chitosan-silver triflate (CSA6) film as depicted in figure 4.4. This is due to the fact that silver nanoparticle reflection planes can be observed above 30°. The four diffraction peaks above 37° (2θ = 38°, 44°, 65° and 78°), correspond to the (111), (200), (220) and (311) reflections of the crystalline planes and they indicate the formation of silver particles with face centered cubic structure and confirm the Ag ion reduction and silver nanoparticle growth [Hu et al., 2007]. These crystalline peaks can also be observed for chitosan-silver triflate (CSA6) at room temperature as shown in Fig.4.2 but the intensity is very small. It can be noticed that the intensity of crystalline plane (111) at 333 K increased at 393 K.
**Figure 4.4** X-ray diffraction pattern of chitosan-silver triflate complex (CSA6) at (a) 333 K, (b) 363K and (c) 393 K.

### 4.2.2 UV-vis and TEM analysis of SPE based on CS:AgTf

To confirm that silver particles have formed, UV-vis absorption spectroscopy and TEM were carried out. UV-vis absorption spectroscopy is a simple and easy method to detect
the presence of silver particles [Kim et al., 2003, Gautam and Ram, 2010]. Fig. 4.5 shows the UV-vis absorption spectra of pure chitosan and chitosan-silver triflate (CSA6) solid electrolyte at ambient temperature (303 K). It can be seen from the figure that pure chitosan has no absorption peak in the region 400 nm to 500 nm, while a broad absorption peak with a maximum at 431 nm was observed for chitosan-silver triflate (CSA6) solid electrolyte. It is generally accepted that an absorption band that peaks between 420 nm and 520 nm is related to the formation of silver metal particles and its height gives information on the concentration of silver metal particles [Kim et al., 2008, Liu et al., 2009].

![Figure 4.5 UV-vis spectra for (a) pure chitosan and (b) chitosan-AgCF$_3$SO$_3$ (CSA6).](image)
Fig. 4.6 shows the UV-vis absorption spectra for chitosan:AgCF$_3$SO$_3$ (CSA6) solid electrolyte at different temperatures. It can be seen that the height of the peaks increases from 0.61 at 303 K to 1.11 at 393 K with increasing temperature, implying an increasing amount of Ag nanoparticles [Kim et al., 2008, Liu et al., 2009]. This result indicates the fact that temperature has a great effect on silver ion reduction to silver nanoparticle in chitosan based solid polymer electrolytes.

![Figure 4.6 UV-vis spectra of chitosan-AgCF$_3$SO$_3$ (CSA6) at different temperatures](image)

Finally, transmission electron microscopy (TEM) was used for visual observation of silver particles in the present system. The TEM image in Figure 4.7 reveals that the silver particles are of nanosize and exists in the form of clusters.
4.2.3 SEM and EDX analysis of SPE based on CS:AgTf

Recently Wei et al., (2009), characterized the silver nanoparticle using SEM and EDX analysis. The morphology and surface composition of silver polymer electrolyte membrane were characterized by scanning electron microscopy (SEM) and energy dispersive X-rays (EDX) to further confirm the formation of metallic silver nanoparticles in the chitosan:AgCF$_3$SO$_3$ film. Figure 4.8(a-e) shows the surface morphology and EDX analysis of all CS:AgTf compositions. These electron images were taken at 500× magnification and show some white cluster and aggregated particles. They can be ascribed to the leakage of silver nanoparticles to the surface of silver polymer electrolyte membrane, which is consistent with the existence of silver nanoparticles investigated, by XRD, UV-vis and TEM method. EDX was used to
demonstrate the metallic silver peak in this system which is usually appeared between 3-3.6 keV.
Figure 4.8 Scanning electron microscopy (SEM) image for (a) CSA2, (b) CSA3, (c) CSA4, (d) CSA5, (e) CSA6 and (f) EDX for spot in box 1.
The EDX spectrum for box 1 in Fig.4.8(e) exhibit an obvious peak for metallic Ag-nanoparticles as shown in figure 4.7 (f). The aggregation of silver nanoparticles on the solid electrolyte surface in the form of white clusters was confirmed by a sharp intense peak in EDX spectrum from 3 to 3.5 keV as shown in Fig. 4.8(f). Similar behavior was reported by Wei et al., (2009) for chitosan:AgNO₃. The significant SEM and EDX results demonstrate the fact that chitosan:AgCF₃SO₃ membrane can be used to prepare silver nanoparticles.

4.3 Structural and morphological analysis of NCPEs based on (1-x)(0.9CS:0.1AgTf)-xAl₂O₃ (0.02 ≤ x ≤ 0.1)

4.3.1 XRD analysis of NCSPE based on (1-x)(0.9CS:0.1AgTf)-xAl₂O₃ (0.02 ≤ x ≤ 0.1)

Figure 4.9 shows several crystalline peaks at around 32°, 34.4°, 36°, 39°, 41°, 45.7°, 61°, and 67.1° for pure Al₂O₃. The X-ray diffraction pattern of the Al₂O₃ nanoparticles depicted in Fig 4.9 is very similar to the Al₂O₃ pattern reported in the literature [Ahmad and Agnihotry, 2009].

Figure 4.9 XRD patterns of pure Al₂O₃ nanoparticles.
To examine the effect of \( \text{Al}_2\text{O}_3 \) nanoparticles on the crystalline structure of solid polymer electrolyte based on CS:AgTf (CSA6), XRD was carried out. Figure 4.10 (a-f) shows the XRD pattern of CS:AgTf (CSA6) SPE and \((1-x)(0.9\text{CS}:0.1\text{AgTf})-x\text{Al}_2\text{O}_3\) \((0.02 \leq x \leq 0.1)\) composite films. It can be clearly seen that the halo of the CSA6 is more broadened with the addition of \( \text{Al}_2\text{O}_3 \) from 2 to 4 wt.%. However, from 6 to 10 wt.% the crystallinity increases again. It is interesting to note that the small peak at \(2\theta = 38^\circ\) in CS:AgTf (CSA6) due to silver nanoparticles has almost disappeared in all \((1-x)(0.9\text{CS}:0.1\text{AgTf})-x\text{Al}_2\text{O}_3\) \((0.02 \leq x \leq 0.1)\) composite films. The peaks at \(45.6^\circ\) and \(67.2^\circ\) in all composite films are due to the \( \text{Al}_2\text{O}_3 \) nanoparticle crystalline peaks (see Fig. 4.9). Another simple method to investigate the effect of \( \text{Al}_2\text{O}_3 \) nanoparticles on silver ion reduction is UV-vis.

![Figure 4.10 X-ray diffratogram of (a) CSA6, (b) CSNA1, (c) CSNA2, (d) CSNA3, (e) CSNA4 and (f) CSNA5.](image)
The crystallite size (coherent length) of the NCPEs has also been calculated using the Debye–Scherrer formula to demonstrate the effect of Al$_2$O$_3$ nano-particles on the crystalline region of SPE (CSA6). Figure 4.11 shows the gaussian fitting on the CSNA2 (4 wt.%), CSNA4 (8 wt.%) and CSNA5 (10 wt.% Al$_2$O$_3$) NCPE samples. It can be observed that the halo of CSNA2 is more broadened compared to CSNA4 and CSNA5 halo. Crystalline peaks at 45.6 and 67.2° can be seen for CSNA5 which is attributable to pure Al$_2$O$_3$ nanoparticles (see Fig. 4.9). In Table 4.2 the calculated FWHM and crystallite size are listed for CSNA2, CSNA4 and CSNA5 samples. The large FWHM and small crystallite size (L) values reveal that CSNA2 is more amorphous. These results reveal that fillers have a significant effect on the crystalline phases of solid polymer electrolytes. Other researchers also used the crystallite size or coherent length study to observe the effect of inorganic filler on the crystalline phase of nano-composite solid polymer electrolytes [Aravindan et al., 2009]. The non existence of chitosan crystalline peak from $2\theta = 5^\circ$ to $2\theta = 35^\circ$, reveals the complete amorphous nature of the samples.
Figure 4.11 Gaussian fitting of XRD for (a) CSNA2 (b) CSNA4 and (c) CSNA5 samples.

Table 4.2 $\theta^\circ$, FWHM and crystallite size (L) for CSNA2, CSNA4 and CSNA5 NCPEs.

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>$\theta^\circ$ (degree)</th>
<th>FWHM (rad)</th>
<th>L (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSNA2</td>
<td>19.7</td>
<td>0.167467</td>
<td>8</td>
</tr>
<tr>
<td>CSNA4</td>
<td>20.1</td>
<td>0.129089</td>
<td>10.9</td>
</tr>
<tr>
<td>CSNA5</td>
<td>20.1</td>
<td>0.137811</td>
<td>10</td>
</tr>
</tbody>
</table>
4.3.2 UV-vis analysis of NCPE based on \((1-x)(0.9\text{CS:0.1AgTf})-x\text{Al}_2 \text{O}_3(0.02 \leq x \leq 0.1)\)

To demonstrate the effect of \(\text{Al}_2 \text{O}_3\) nanoparticles on silver ion reduction UV-vis were carried out. UV-vis spectra for all nanocomposite films are shown in Fig. 4.12 (a-e). It is clear that with increasing \(\text{Al}_2 \text{O}_3\) nanoparticles the surface plasmon band of silver nanoparticles decreased compared to CSA6 system (see Fig. 4.5(b)). These results indicate the fact that \(\text{Al}_2 \text{O}_3\) nanoparticles prevented silver ion reduction.
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**Graph C:**
- Absorbance (a.u) vs. Wavelength (nm)
- Data points at wavelengths 300, 350, 400, 450, 500, 550, 600, 650, 700

**Graph D:**
- Absorbance (a.u) vs. Wavelength (nm)
- Data points at wavelengths 300, 350, 400, 450, 500, 550, 600, 650, 700
4.3.3 SEM and EDX analysis of NCPE based on (1-x)(0.9CS:0.1AgTf)-xAl$_2$O$_3$ (0.02 ≤ x ≤ 0.1)

To confirm the hindrance of silver ion reduction by Al$_2$O$_3$ nanoparticles, the morphology and surface composition of all NCPEs were taken by scanning electron microscopy (SEM) and energy dispersive X-rays (EDX). Figure 4.13(a-e) shows the surface morphology of all compositions of (1-x)(0.9CS:0.1AgTf)-xAl$_2$O$_3$ (0.02 ≤ x ≤ 0.1). These electron images were taken at 500× magnification and show some white cluster and aggregated particles for high filler concentrations. The SEM and EDX results demonstrate the fact NCPEs morphology is completely different from that obtained for CS:AgTf SPEs. From the EDX result it is clear that silver nanoparticle peak is very small and the main peak is due to Al$_2$O$_3$ nanoparticles which are distributed in the form of clusters on the surface of NCPEs. Thus, the UV-vis, SEM and EDX results are supported the XRD results.
Figure 4.13 Scanning electron microscopy (SEM) image for (a) CSNA1, (b) CSNA2, (c) CSNA3, (d) CSNA4, (e) CSNA5 and (f) EDX for spot in box 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>39.48</td>
<td>44.83</td>
</tr>
<tr>
<td>N K</td>
<td>30.13</td>
<td>29.63</td>
</tr>
<tr>
<td>O K</td>
<td>29.20</td>
<td>24.89</td>
</tr>
<tr>
<td>Al K</td>
<td>1.18</td>
<td>0.60</td>
</tr>
<tr>
<td>S K</td>
<td>0.30</td>
<td>0.13</td>
</tr>
<tr>
<td>Ag L</td>
<td>0.59</td>
<td>0.07</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>
4.4 Structural and morphological analysis of SPEs based on CS:NaTf

4.4.1 XRD analysis of SPE based on CS:NaTf

In order to investigate the effect of NaCF$_3$SO$_3$ on the structure of chitosan-based polymer electrolyte, X-ray diffraction of pure NaCF$_3$SO$_3$, pure chitosan film and their complexes have been performed. Fig. 4.14 shows the X-ray diffraction patterns of pure NaCF$_3$SO$_3$. The crystalline peaks of pure NaCF$_3$SO$_3$ salt can be detected at $2\theta = 8.5^\circ$, 9.95°, 16.8°, 22.15°, 26.25°, 32.9°, 35.6°, and 40.9°. This is in good agreement with the diffractogram of pure NaCF$_3$SO$_3$ salt as reported in the literature [Osman et al., 2010].

![XRD pattern of pure NaCF$_3$SO$_3$ salt.](image)

The diffractograms of the pure chitosan film and chitosan:NaCF$_3$SO$_3$ complexes, are illustrated in Fig. 4.15.
Pure chitosan (CSB1) is semi-crystalline. In the XRD pattern of pure chitosan, the broad peaks at around $2\theta = 15.5^\circ$ and $21^\circ$, indicate the average intermolecular distance of the crystalline part of pure chitosan membrane [Fadime et al., 2008]. This rigid crystalline structure of chitosan is mainly maintained by intramolecular and intermolecular hydrogen bonds [Wan et al., 2006]. It can be noticed that, when 2 wt. % of NaCF$_3$SO$_3$ is added to chitosan the intensity of the crystalline peaks of pure chitosan decreased and the peak at $2\theta \sim 15.5^\circ$ has broadened, Fig 4.15(b). An obvious peak at $2\theta \sim 11.6^\circ$ for chitosan added with 4, 6, 8 and 10 wt.% of NaCF$_3$SO$_3$ can be ascribed to the shift of 10.6° peak of pure chitosan (Fig. 4.15(a)). On addition of more salt to chitosan, the main crystalline peak of pure chitosan at 20.9° shifts to 22.8° and the peak at 17.2° shifts to 18.4° in CSB2, CSB3, CSB4, CSB5 and CSB6 SPE samples. Hashmi and
Chandra (1995), reported that these peak shifting may be due to some long-range order set by the presence of ion multiples. According to Sanders et. al., (2003), the shifting of the peaks is attributed to formation of polymer-salt complexes rather than that of pure NaCF$_3$SO$_3$ salt. The shifting of peaks is an indication that some long-range order has been set by the formation of chitosan-salt complexes at salt concentration greater than 2 wt. % of NaCF$_3$SO$_3$.

Figure 4.16 (a-b) depicts the gaussian fitting on CSB2 and CSB6 SPE samples. The obtained FWHM for these samples were presented in Table 4.3. The CSB6 sample exhibits the largest FWHM value. The calculated crystallite size in Table 4.3 reveals that the CSB6 sample is more amorphous. Thus the calculated crystallite size for solid polymer electrolytes based on CS:NaTf reveal that the crystalline region of chitosan (CS) is greatly affected by the salt (NaTf). The decrease of degree of crystallinity with addition of NaTf salt is due to the disruption of chitosan crystalline phase.
Figure 4.16 Gaussian fitting of XRD for (a) CSB2, (b) CSB5 and (c) CSB6 samples.
Table 4.3 $2\theta$, FWHM, crystallite size ($L$) and degree of crystallinity ($\chi$) for CSB2, CSB5 and CSB6 SPEs.

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>$2\theta$ (degree)</th>
<th>FWHM (rad)</th>
<th>$L$ (Å)</th>
<th>Degree of Crystallinity (%)</th>
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<td>21.1</td>
<td>0.096468</td>
<td>15</td>
<td>16.3</td>
</tr>
<tr>
<td>CSB5</td>
<td>21.2</td>
<td>0.129088</td>
<td>14</td>
<td>13.6</td>
</tr>
<tr>
<td>CSB6</td>
<td>21.2</td>
<td>0.108156</td>
<td>13</td>
<td>10.8</td>
</tr>
</tbody>
</table>

4.4.2 SEM analysis of SPE based on CS:NaTf

The surface morphology of CS:NaTf SPEs is shown in Fig. 4.17(a-e). From the SEM images it is clear that the surface is smooth and almost homogeneous. The SEM images reveal that there is no phase separation or clusters in CS:NaTf complexes. These results indicated a complete dissolution of NaTf salt in chitosan (CS) host polymer.
Figure 4.17 Scanning electron microscopy (SEM) image for (a) CSB2, (b) CSB3, (c) CSB4, (d) CSB5 and (e) CSB6.
4.5 Structural and morphological analysis of NCPEs based on \((1-x)(0.9\text{CS:0.1NaTf})-x\text{Al}_2\text{O}_3\) \((0.02 \leq x \leq 0.1)\)

4.5.1 XRD analysis of NCPE based on \((1-x)(0.9\text{CS:0.1NaTf})-x\text{Al}_2\text{O}_3\) \((0.02 \leq x \leq 0.1)\)

Figure 4.18 displays the XRD pattern of CS:NaTf (CSB6) with various concentrations of \(\text{Al}_2\text{O}_3\) (2 to 10 wt.%). It can be seen that with addition of \(\text{Al}_2\text{O}_3\) nanoparticles to CS:NaTf (CSB6) the crystalline peaks of CSB6 SPE become broader and less sharp. From 6 to 10 wt.% of \(\text{Al}_2\text{O}_3\) nanoparticles two new crystalline peaks appeared at 45.6° and 67.1° which is attributable to pure \(\text{Al}_2\text{O}_3\) nanoparticle crystalline peaks (see Fig. 4.9). On addition of more than 4 wt.% \(\text{Al}_2\text{O}_3\) the overall crystalline structure of NCPEs increased.

![Figure 4.18 X-ray diffratogram of (a) CSB6, (b) CSNB1, (c) CSNB2, (d) CSNB3, (e) CSNB4 and (f) CSNB5.](image-url)
Figure 4.19 shows the gaussian fitting on CSNB2, CSNB3 and CSNB5 samples. The calculated FWHM and crystallite size (Table 4.4) reveal that CSNB2 is more amorphous compared to CSNB3 and CSNB5. The sharp peak at 21.2° for CSNB5 reveals the increase of crystalline region at higher Al₂O₃ concentration. The crystalline peaks at 45.6° and 67.1° for CSNB5 sample can be ascribed to Al₂O₃ nanoparticles crystalline peaks (see Fig. 4.9). The higher the amorphous nature of the electrolyte results in higher conductivity of the sample. The small value in crystallinity for CSNB2 sample can be attributed to the interaction between polymer chains with filler which prevents the polymer chain reorganisation. Above 4 wt.% of Al₂O₃ in the chitosan matrix results in an increase in L and χ. This is ascribed to the increase of aggregation of particles which increases the crystallinity of the membrane [Saikia et al., 2008].
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Figure 4.19 Gaussian fitting of XRD for (a) CSNB2, (b) CSNB3 and (c) CSNB5 samples.

Table 4.4, 2θ, FWHM, crystallite size (L) and degree of crystallinity (χ) for CSNB2, CSNB3 and CSNB5 NCPEs.

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>2θ (degree)</th>
<th>FWHM (rad)</th>
<th>L (Å)</th>
<th>Degree of Crystallinity (%)</th>
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</thead>
<tbody>
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<td>9.3</td>
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<td>CSNB5</td>
<td>21.2</td>
<td>0.099433</td>
<td>14</td>
<td>14.4</td>
</tr>
</tbody>
</table>
4.5.2 SEM and EDX analysis of NCPE based on (1-x)(0.9CS:0.1NaTf)-xAl$_2$O$_3$ (0.02 ≤ x ≤ 0.1)

To support the XRD results SEM and EDX were carried out on the NCPEs. From Fig 4.20, it is obvious that the NCPEs containing 2 and 4 wt. % are almost smooth and Al$_2$O$_3$ nanoparticles are well distributed. However, from 6 to 10 wt. % of Al$_2$O$_3$, the surface morphology shows Al$_2$O$_3$ aggregates on the top surface. As a whole, the distribution of Al$_2$O$_3$ nanoparticles are homogeneous and uniform when the amount of filler is less than 6 wt. %. It can be seen that from the EDX result that the main peak is attributable to Al$_2$O$_3$. Thus, from these results it can be understood that the increase in crystallinity as observed in Fig.4.18 at high filler concentration can be attributable to the aggregation of Al$_2$O$_3$ nanoparticles as demonstrated by the SEM and EDX results which strongly supports the XRD pattern for these NCPEs.
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b

c

Parameters: EHT = 10.00 kV, Probe = 100 pA, Mag = 500X, Det = SE1, WD = 16 nm, Date = Jan-1988
Figure 4.20 Scanning electron microscopy (SEM) image for (a) CSNB1, (b) CSNB2, (c) CSNB3, (d) CSNB4, (e) CSNB5 and (f) EDX for spot in box 1.

4.6 Structural and morphological analysis of SPEs based on CS:LiTf

4.6.1 XRD analysis of SPEs based on CS:LiTf

In this system, XRD was performed to show the complex formation occurrence between LiCF$_3$SO$_3$ and chitosan. The crystalline peaks of pure LiCF$_3$SO$_3$ can be detected at $2\theta = 16.5^\circ$, $19.75^\circ$, $20.4^\circ$, $22.55^\circ$, $25.3^\circ$, and $33.15^\circ$. The X-ray diffraction pattern and crystalline peaks of the LiCF$_3$SO$_3$ salt (Fig. 4.21) is in good agreement with literature [Osman et al., 2010].
Chapter Four  
Structural and Morphological Study

The diffractograms of the pure chitosan acetate film (CSC1) and chitosan:LiCF$_3$SO$_3$ complexes, are illustrated in Fig. 4.22.

Figure 4.21 X-ray diffraction pattern of pure LiCF$_3$SO$_3$ salt.

Figure 4.22 X-ray diffraction pattern of (a) CSC1 (pure chitosan), (b) CSC2, (c) CSC3, (d) CSC4, (e) CSC5 and (f) CSC6.
It can be seen that, with addition of lithium triflate (LiTf) into chitosan matrix, intensity of the crystalline peaks of pure chitosan decreased drastically (see Fig. 4.22). This indicates the reduction in crystalline region of chitosan matrix. In other words with increasing salt concentration the amorphous domain of the chitosan electrolyte membrane increases. It can be seen that the peak of pure chitosan at 15.5° shifted to 12.6° in CS:LiTf systems.

To observe the effect of LiTf salt on the crystalline structure of chitosan the crystallite size of CS:LiTf electrolytes was calculated using the Debye–Scherrer formula. The gaussian fitting on CSC2 (2 wt.% LiTf), CSC5 (8 wt.% LiTf) and CSC6 (10 wt.% LiTf) SPE samples were shown in Fig. 4.23. The obtained FWHM for these samples were presented in Table 4.5. The CSB6 sample exhibits a largest FWHM value. The calculated crystallite sizes and χ in Table 4.5 reveal that the CSC6 sample is more amorphous. This indicates that the amorphous region can be enhanced with increasing of salt concentration. Thus the obtained FWHM and the calculated crystallite sizes for SPEs (CS:AgTf, CS:NaTf and CS:LiTf) reveal the reduction of crystalline phase of pure chitosan and enhancement of amorphous domain upon the addition of inorganic salts.
Figure 4.23 Gaussian fitting of XRD for (a) CSC2, (b) CSC5 and (c) CSC6 samples.

Table 4.5 2°, FWHM, crystallite size (L) and degree of crystallinity (χ) for CSC2, CSC5 and CSC6 SPEs.

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>2 θ degree</th>
<th>FWHM (rad)</th>
<th>L (Å)</th>
<th>Degree of Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSC2</td>
<td>20.8</td>
<td>0.108679</td>
<td>13</td>
<td>11.8</td>
</tr>
<tr>
<td>CSC5</td>
<td>20.5</td>
<td>0.111993</td>
<td>12.5</td>
<td>10.3</td>
</tr>
<tr>
<td>CSC6</td>
<td>20.3</td>
<td>0.116878</td>
<td>12</td>
<td>9.5</td>
</tr>
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4.6.2 SEM analysis of SPEs based on CS:LiTf

Figure 4.24 shows the surface morphology of CS:LiTf SPEs (CSC2 to CSC6). The SEM characterizations were carried out in order to understand the morphological changes during LiTf addition to chitosan. From the figure it is clear that the surface is smooth and almost homogeneous and there are no clusters on the surface as observed for CS:AgTf systems as a result of silver ion reduction.
4.7 Structural and morphological analysis of NCPEs based on (1-x)(0.9CS:0.1LiTf)-xAl₂O₃ (0.02 ≤ x ≤ 0.1)

4.7.1 XRD analysis of NCPEs based on (1-x)(0.9CS:0.1LiTf)-xAl₂O₃ (0.02 ≤ x ≤ 0.1)

X-ray diffraction analysis was performed to observe the effect of Al₂O₃ filler on the crystalline nature of SPE based on CS:LiTf (CSC6). Its interesting to note that the crystalline nature of NCPEs (Fig. 4.25) is largely reduced compared to SPE (CSC6). In the diffractogram of Fig. 4.25, the crystallinity for 2 and 4 wt.% of Al₂O₃ are largely reduced, however from 6 to 10 wt. % of Al₂O₃ the crystallinity is again increased. The absence of crystalline peaks of pure Al₂O₃ nanoparticles in the 2 and 4 wt.% indicates good dispersion and blending between the polymer electrolyte and the nano Al₂O₃ filler.
The crystalline peaks at 45.7° and 67.2° degree for NCPEs above 4 wt.%, are due to pure Al₂O₃ nanoparticles (see Fig.4.9).

Figure 4.25 X-ray diffractogram of (a) CSC6, (b) CSNC1, (c) CSNC2, (d) CSNC3, (e) CSNC4 and (f) CSNC5.

Figure 4.26 depicts the gaussian fitting on CSNC2, CSNC3 and CSNC 5 samples. The obtained FWHM from gaussian fitting and the calculated crystallite size are presented in Table 4.6. From FWHM, crystallite size (L) and degree of crystallinity (χ) values (Table 4.6), it can be seen that CSNC2 is more amorphous. These results indicate the fact that high Al₂O₃ nanoparticle concentration will increase the crystalline regions as a result of Al₂O₃ nanoparticle aggregation. The additional crystalline peaks at 45.7 and 67.2° for CSNC3 and CSNC5 samples can be ascribed to Al₂O₃ nanoparticle crystalline peaks.
(see Fig. 4.9). Thus from the XRD results of \((1-x)(0.9\text{CS}:0.1\text{AgTf})-x\text{Al}_2\text{O}_3\) \((0.02 \leq x \leq 0.1)\), \((1-x)(0.9\text{CS}:0.1\text{NaTf})-x\text{Al}_2\text{O}_3\) \((0.02 \leq x \leq 0.1)\) and \((1-x)(0.9\text{CS}:0.1\text{LiTf})-x\text{Al}_2\text{O}_3\) \((0.02 \leq x \leq 0.1)\) NCPEs it appeared that \text{Al}_2\text{O}_3\ nanoparticle has a great effect on crystalline phase of SPEs (CS:AgTf, CS:NaTf and CS:LiTf).
Figure 4.26 Gaussian fitting of XRD for (a) CSNC2, (b) CSNC3 and (c) CSNC5 samples.

Table 4.6 2θ, FWHM, crystallite size (L) and degree of crystallinity (χ) for CSNC2, CSNC3 and CSNC5 NCPEs.

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>2θ degree</th>
<th>FWHM (rad)</th>
<th>L (Å)</th>
<th>Degree of Crystallinity (%)</th>
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</thead>
<tbody>
<tr>
<td>CSNC2</td>
<td>21</td>
<td>0.143044</td>
<td>10</td>
<td>8.4</td>
</tr>
<tr>
<td>CSNC3</td>
<td>21.2</td>
<td>0.108156</td>
<td>12</td>
<td>9.7</td>
</tr>
<tr>
<td>CSNC5</td>
<td>20.9</td>
<td>0.1099</td>
<td>13</td>
<td>12.3</td>
</tr>
</tbody>
</table>

4.7.2 SEM and EDX analysis of NCPEs based on (1-x)(0.9CS:0.1LiTf)-xAl₂O₃ (0.02 ≤ x ≤ 0.1)

SEM and EDX are carried out to perform the surface morphology of nano-composite polymer electrolytes based on (1-x)(0.9CS:0.1LiTf)-xAl₂O₃ (0.02 ≤ x ≤ 0.1). Fortunately, the surface morphology is almost smooth and homogeneous for 2 and 4 wt.
% of Al$_2$O$_3$ nanoparticle, as depicted in Fig. 4.27(a-b), which strongly supports the XRD results. However, a large number of white clusters appeared on the surface of NCPEs from 6 to 10 wt.% of Al$_2$O$_3$ nanoparticle (Fig. 4.27(c-e)) indicating that Al$_2$O$_3$ nanoparticles at higher concentrations are not well distributed. Thus, the morphology of NCPEs became rough when the concentration of Al$_2$O$_3$ nanoparticles increased beyond 4 wt.% and these results are in good agreement with the XRD results. The EDX results presented in Fig. 4.27(f), confirms that these white clusters are aggregates of Al$_2$O$_3$ nanoparticles. This again supports the XRD results.
4.8 Summary

The XRD results of CS:AgTf (CSA1 to CSA6), CS:NaTf (CSB1 to CSB6) and CS:LiTf (CSC1 to CSC6) systems reveal the occurrence of complexation between chitosan (CS) and the salts. The deconvolution of the diffractogram of these solid polymer electrolytes (CS:AgTf, CS:NaTf and CS:LiTf) demonstrates the increase of amorphous domain with increasing salt content. The SEM analysis in CS:NaTf and CS:LiTf SPEs reveal smooth surfaces. In CS:AgTf solid polymer electrolyte the XRD results shows the crystalline peak for silver particle. UV-vis, TEM, SEM and EDX results confirmed the formation of silver nanoparticles in the CS:AgTf systems.
The addition of alumina nanoparticles (up to 4 wt.% $\text{Al}_2\text{O}_3$) for the highest amorphous system (small crystallite size) of solid polymer electrolytes (CSA6, CSB6 and CSC6) results in the increase of amorphous region. Further incorporation of alumina nanoparticles (6 to 10 wt.% $\text{Al}_2\text{O}_3$) to SPEs results in crystallinity increase (large crystallite size). The morphological (SEM and EDX) analysis well supported the XRD results in NCPEs $\{(1-x)(0.9\text{CS}:0.1\text{AgTf})_x\text{Al}_2\text{O}_3 \ (0.02 \leq x \leq 0.1), \ (1-x)(0.9\text{CS}:0.1\text{NaTf})_x\text{Al}_2\text{O}_3 \ (0.02 \leq x \leq 0.1) \}$ and $\{(1-x)(0.9\text{CS}:0.1\text{LiTf})_x\text{Al}_2\text{O}_3 \ (0.02 \leq x \leq 0.1)\}$. The XRD, UV-vis, SEM, and EDX results for $\{(1-x)(0.9\text{CS}:0.1\text{AgTf})_x\text{Al}_2\text{O}_3 \ (0.02 \leq x \leq 0.1)\}$ NCPE reveal that $\text{Al}_2\text{O}_3$ addition prevents silver ion reduction to silver nanoparticles.