CHAPTER 4

EFFECT OF BIO-NANOFILLERS ON STRUCTURAL, THERMAL, ELECTRICAL, ELECTROCHEMICAL AND INTERFACIAL PROPERTIES OF (PEO-LiCF₃SO₃) BASED COMPOSITE POLYMER ELECTROLYTES

In this chapter, we are presenting the results obtained for the three classes of polymer electrolytes prepared in the present study. The nanocomposite polymer electrolytes (NCPEs) were prepared using polyethylene oxide (PEO) as the polymer host and lithium triflate (LiTf) as the salt. The nanofillers used were nanochitosan (NC), chitin nanofiber (CNF) and nano hydroxy apatite (nHAp). The concentration of lithium salt was optimized as 5 wt%. The concentration (in wt %) of PEO and NC/CNF/nHAp are given in Tables 4.1/4.2/4.3 respectively. The solvent used was tetrahydrofuran (THF). All the polymer electrolytes were prepared by membrane hot press. The resultss are presented herein.

Table 4.1 Compositions of PEO, LiTf and NC

<table>
<thead>
<tr>
<th>Sample code</th>
<th>PEO (wt %)</th>
<th>LiCF₃SO₃ (wt %)</th>
<th>NC (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1</td>
<td>95</td>
<td>5</td>
<td>--</td>
</tr>
<tr>
<td>NC1</td>
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<td>5</td>
<td>5</td>
</tr>
<tr>
<td>NC2</td>
<td>85</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>NC3</td>
<td>80</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>NC4</td>
<td>75</td>
<td>5</td>
<td>20</td>
</tr>
</tbody>
</table>
Table 4.2 Compositions of PEO, LiTf and CNF

<table>
<thead>
<tr>
<th>Sample code</th>
<th>PEO (wt %)</th>
<th>LiCF$_3$SO$_3$ (wt %)</th>
<th>CNF (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNF1</td>
<td>90</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>CNF2</td>
<td>85</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>CNF3</td>
<td>80</td>
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<td>15</td>
</tr>
<tr>
<td>CNF4</td>
<td>75</td>
<td>5</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 4.3 Compositions of PEO, LiTf and nHAp

<table>
<thead>
<tr>
<th>Sample code</th>
<th>PEO (wt %)</th>
<th>LiCF$_3$SO$_3$ (wt %)</th>
<th>nHAp (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA1</td>
<td>90</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>HA2</td>
<td>85</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>HA3</td>
<td>80</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>HA4</td>
<td>75</td>
<td>5</td>
<td>20</td>
</tr>
</tbody>
</table>

4.1 RESULTS AND DISCUSSIONS

4.1.1 X-ray diffraction (XRD) studies

XRD measurements were done to examine the crystallinity of the polymer electrolyte relative to the host polymer. XRD patterns of the polymer electrolytes are presented in Figure 4.1 (a-e). It represents the XRD patterns of PEO, PE1, NC1, NC2 and NC3 nanocomposite polymer electrolytes (NCPEs). The diffraction peaks at $2\theta =19.51^\circ$ and $23.73^\circ$ correspond to the prominent peaks of crystalline PEO (JCPDS file No: 39-1894). On the other hand, the diffraction peaks at $15.19^\circ$ and $23.12^\circ$ correspond to the (120) and (220) reflections of chitosan (Zhi-Hai Huang et al 2008 and Xiaohui et al 2004). The fundamental peaks of lithium triflate are absent in all the
dифрактограмм. Это показывает, что литий-соль полностью растворена в полимерной матрице и образовала полимер-литиевые комплексы (Angulakshmi et al 2012 и Yogesh Kumar et al 2011). В Figure 4.1 (c-e), наблюдается, что интенсивность кристаллических пики уменьшилась и расширилась при включении NC. Однако, пики соответствующие читосан остаются неизменными. Эта наблюдение подразумевает, что полимер подвергся значительной структурной перестройке из-за включения NC и литий-соль. Чтобы быть конкретным, включение наполнителя, имеется уменьшение в кристалличности полимера, увеличивая его ионную проводимость.

Figure 4.1 The XRD patterns of (a) pure PEO, (b) PE1, (c) NC1, (d) NC2 and (e) NC3
The XRD pattern for synthesized CNF was already reported in the literature (Angulakshmi et al 2013). The XRD pattern of CNF incorporated polymer electrolytes CNF1 (5%), CNF2 (10%) and CNF3 (15%) were shown in Figure 4.2 panels (a-c). The peak at an angle 2θ = 10.1°, 22.5°, 25°, 17.9° and 29.4° corresponds to (020), (101), (130), (110) and (202) reflection planes of CNF respectively. The incorporation of CNF in the polymer matrix results in diminished peak intensity and the peak becomes broadened. This is due to the fact that there was reduction in crystalline nature of polymer by incorporation of filler. Hence, the incorporation of high filler content (wt %) enhances the amorphous region of polymer host as similar to that of NC based polymer electrolytes.

![XRD patterns](image)

**Figure 4.2 (a-c) XRD patterns of (a) CNF1, (b) CNF2 and (c) CNF3**

Similarly, the incorporation of nHAp nanoparticles in polymer electrolytes exhibits characteristic peaks at 2θ = 31°91', 33°25', 39°51', 47°11' and 65° corresponds to (211), (300), (310), (222) and (304) reflection planes.
of HAp respectively. The different diffraction peaks in XRD pattern are indexed and compared with earlier reports (Kailasanathan et al. 2012 and Baskaran et al. 2006). It is observed from the Figure 4.3 (b-d), the intensity of crystalline peaks decreases with incorporation of nHAp. The peak broadening in the diffractogram is the clear evidence for polymer segmental motion enhancement (amorphous nature) which is responsible for ionic conductivity.

![XRD patterns](image)

**Figure 4.3 XRD patterns of (a) PE1, (b) HA1, (c) HA2 and (d) HA3**

### 4.1.2 DSC analysis

Thermal analysis using DSC was performed in order to observe the reduction in melting temperature ($T_m$) of nanofillers incorporated polymer electrolytes. Figure 4.4 (a-d) shows the DSC thermogram of filler free polymer electrolyte PE1 and various compositions of NC incorporated
polymer membranes NC1, NC2 and NC3. The PE1 shows a sharp endothermic peak at 66 °C which is due to the melting temperature of polymer PEO. The incorporation of NC in the polymer matrix was found to decrease the melting temperature of PEO as showed from Figure 4.4 (b-d). The NC incorporation in the polymer matrix results in the broadening of the melting endotherm with an apparent decrease in the heat of fusion ($\Delta H_f$). The crystallinity ($\alpha$) was determined from the DSC curves using the relation (Equation 4.1),

$$\alpha = \frac{\Delta H_f}{\Delta H_{f100\%}}$$  \hspace{1cm} (4.1)

The value of $\Delta H_{f100\%}$ for pure PEO = 213.7 J/g (Capiglia et al 2003 and Junichi Kadokawa et al 2011). The value of $\Delta H_f$ was obtained from the DSC curves recorded in the present study.

Figure 4.4 The DSC thermogram of (a) PE1, (b) NC1, (c) NC2 and (d) NC3
The percentage of crystallinity was minimum for the sample NC2 (which was shown in Table 4.4). The reduction of melting peak ($T_m$) in NC incorporated membrane might be due to the enhancement of polymer segmental motion as well as increase in amorphous nature induced by the filler-polymer interaction of polymer electrolyte. Hence, the movement of ions inside the polymer matrix leads to the increase of conductivity. This is also supported by the observation made in the ionic conductivity studies explained later in this chapter.

Table 4.4 $T_m$ and crystallinity of PE1 and NC incorporated NCPEs NC1, NC2 and NC3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallinity ($\alpha$) (%)</th>
<th>Melting temperature ($T_m$) ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1</td>
<td>100</td>
<td>66.2</td>
</tr>
<tr>
<td>NC1</td>
<td>73.1</td>
<td>62.3</td>
</tr>
<tr>
<td>NC2</td>
<td>68.2</td>
<td>61.8</td>
</tr>
<tr>
<td>NC3</td>
<td>69.8</td>
<td>60.2</td>
</tr>
</tbody>
</table>

The DSC thermogram of CNF incorporated polymer electrolytes are shown in Figure 4.5(a-c). The endothermic peak for pure PEO shows the transition from 66 to 59 $^\circ$C upon the addition of 5 wt % of CNF. The $T_m$ value continues to decrease as CNF gets incorporated (shown in Table 4.5). This observation shows the reduction in $T_m$ value by the incorporation of CNF. The degree of crystallinity of the electrolyte decreases with the wt % of the CNF, which causes an increase in the amorphous phase. The polymeric chain in the amorphous phase is more flexible and provides better segmental motion of the polymer. The reduction of $T_m$ and $\alpha$ suggested that the interaction between the polymer host backbone and CNF affects the main chain dynamics of the polymer. This is due to the coordination bonds between ether units of PEO.
and CNF. It interrupts the packing of PEO molecules and decreased the degree of crystallinity.

Table 4.5 $T_m$ and crystallinity of PE1 and CNF incorporated NCPEs CNF1, CNF2 and CNF3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallinity ($\alpha$) (in %)</th>
<th>Melting temperature ($T_m$) (in °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1</td>
<td>100</td>
<td>66.2</td>
</tr>
<tr>
<td>CNF1</td>
<td>72.2</td>
<td>59.9</td>
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<tr>
<td>CNF2</td>
<td>68.1</td>
<td>58.8</td>
</tr>
<tr>
<td>CNF3</td>
<td>69.5</td>
<td>57.6</td>
</tr>
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</table>

![Figure 4.5 The DSC thermogram of (a) CNF1, (b) CNF2 and (c) CNF3](image)
Likewise, the effect of nHAp on crystallinity of PEO-LiTf complexes is studied by DSC thermograms and shown in Figure 4.6 (a-c). The incorporation of nHAp in the polymer matrix significantly reduces the crystalline nature of PEO and \( T_m \) also decreases (up to 59 °C) as shown in Figure 4.6 (a- c) and Table 4.6. The reduction of \( T_m \) and \( \alpha \) suggests that the interaction between the polymer host backbone and nHAp affected the main chain dynamics of the polymer and enhances the polymer segmental chain motion thereby enhancing the conductivity.

Figure 4.6 The DSC thermogram of (a) HA1, (b) HA2 and (c) HA3
Table 4.6 $T_m$ and crystallinity of PE1, HA1, HA2 and HA3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallinity ($\alpha$) (%)</th>
<th>Melting temperature ($T_m$) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1</td>
<td>100</td>
<td>66.2</td>
</tr>
<tr>
<td>HA1</td>
<td>78</td>
<td>62.2</td>
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<tr>
<td>HA2</td>
<td>72</td>
<td>61.8</td>
</tr>
<tr>
<td>HA3</td>
<td>74.5</td>
<td>59.9</td>
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4.1.3 Fourier Transform Infra Red (FT-IR) analysis

The complexation behavior of lithium salt and polymer system with nanofillers can be identified from FT-IR spectra. In Figure 4.7, panels (a-c) show the FT-IR spectra of PEO, LiTf and PE1 complexes respectively. The peaks (Figure 4.7, panel (a)) that appear at 2888 and 2740 cm$^{-1}$ in pure PEO correspond to symmetrical and asymmetrical stretching modes of CH$_2$- group. Moreover, the peaks found at 1260, 1240 and 1155 cm$^{-1}$ are attributed to asymmetric CH$_2$-twisting, symmetric CH$_2$-twisting modes and C-O-C asymmetric stretching mode of pure PEO respectively (Lee et al 2013). The incorporation of LiTf in the polymer matrix can be identified by the peaks noted at 1033 and 638 cm$^{-1}$ which corresponds to $\nu_{str}$(SO$_3^-$) and $\delta$(SO$_3^-$) (Figure 4.7 (b)) (Leiling Yang et al 1990). The shifting of peaks from 1144 to 1090 cm$^{-1}$ indicates that the addition of lithium salt has made appropriate changes in the polymer matrix as noted in Figure 4.7, panel (c). Furthermore, the peak shifts from 953 cm$^{-1}$ (pure PEO) to 950cm$^{-1}$ (PE1) indicates the complexation behavior of polymer electrolyte ((Ramesh et al 2007 and Krawiec et al 1995). Figure 4.8 represents the FT-IR spectra of NC, CNF and nHAp. The characteristic peaks that observed at 889, 1582, 1360-1020 and 3300-3740 cm$^{-1}$ correspond to polysacchararide, N-H stretching, C-N stretching and O-H group of NC respectively. In the case of CNF, the characteristic peaks at
3740, 2888, 1732 and 1582 cm⁻¹ have assigned to O-H stretching, C-H stretching, N-H stretching and C=O hydrogen bonded to N-H of neighbourhood inter sheet chain respectively. The peaks at 1340 and 880 cm⁻¹ indicate the presence of polysaccharide group (Figure 4.8). The characteristic bands in the region 3451, 629 and 879 cm⁻¹ are allocated to OH stretching, structural OH and PO₄²⁻ (stretching) respectively.

Figure 4.7 FT-IR spectra of (a) PEO, (b) LiTf and (c) PE1
The incorporation of NC in the polymer electrolyte was confirmed by the shifting of peaks from 889 to 839, 1360 to 1351 and 3739 to 3733 cm\(^{-1}\) (Figure 4.9, panel (a)). The obtained results are in agreement with the earlier reported results (Manuel Stephan et al 2006). Similarly, the incorporation of CNF causes some appropriate changes in polymer matrix. It is evidenced that, the shifting of peaks from 2880, 1732, 1582 and 880 cm\(^{-1}\) to 2885, 1728, 1594 and 884 cm\(^{-1}\) respectively as given in Figure 4.9 panel (b). In Figure 4.8, panel (c) shows the FT-IR spectrum of NC2. The incorporation of nHAp in the polymer matrix is confirmed by the shifting of peaks from 3451 to 3466 cm\(^{-1}\) and 1089 to 1098 cm\(^{-1}\) which was shown in Figure 4.9, panel (c).

![FT-IR spectra of (a) NC, (b) CNF and (c) nHAp](image-url)
Figure 4.9 FT-IR spectra of various nanofillers incorporated NCPEs (a) NC2, (b) CNF2 and (c) HA2.

4.1.4 SEM studies of NCPEs

The SEM images obtained for the surface of the polymer electrolytes incorporated with the bio-nanofillers (viz., NC (panel b), CNF (panel c) and nHAp (panel d)) NCPEs are presented in Figure 4.10.
Figure 4.10 The SEM image of (a) PE1, (b) NC2, (c) CNF2 and (d) HA2

The SEM image of PE1 shows cryo-fractured structure with non uniform morphology and that of NC incorporated electrolyte NC2 shows uniform homogeneous cloudy structure with the average particle size of 10 μm (panel b in Figure 4.10). The uniform surface morphology of high filler content electrolytes (10 wt %) may be due to uniform distribution of nanofiller as well as good miscibility of nanofiller in the polymer matrix. The smooth surface morphology is attributed to reduction in crystalline nature of PEO due to cross-linking with cations of both lithium ion and NC. This crosslinking leads to formation of rigid polymer-filler network. The CNF incorporated NCPE (CNF2) shows branches like surface, which indicate
sufficiently good miscibility of CNF with PEO and lithium salt. The branches like morphology may owe to the fact that the CNF particles are identically distributed throughout the matrix of the polymer and attributed to the formation of rigid polymer-filler network (panel c). Similarly, the SEM image of HA2 shows randomly interconnected wrinkle wave structure on the surface of the electrolyte as shown in panel d.

4.1.5 Ionic conductivity

The ionic conductivity depends on overall mobility of ion and polymer which can be determined by free volume around the polymer chain. The ionic conductivity (\(\sigma\)) of the prepared polymer electrolytes is calculated by means of following (Equation 4.2)

\[
\sigma = \frac{I}{R_b A}
\]  

(4.2)

where \(t\) and \(A\) are the thickness and area of the polymer electrolyte in contact with the electrodes respectively. Thickness of the electrolyte was measured using a digital micrometer screw gauge. \(R_b\) represents the bulk resistance of the polymer electrolyte. According to Vogel-Tammann-Fulcher relation (VTF), the conductivity increases with increase in temperature (Equation 4.3)

\[
\sigma = \left(\frac{A}{T^{1.5}}\right) e^{ \frac{B}{T-T_g} }
\]  

(4.3)

where \(A\) and \(B\) are constants. \(T\) and \(T_g\) represents absolute and glass transition temperature of the material. The constant \(A\) in VTF equation is related to number of charge carriers and \(B\) is related to activation energy of ion transport associated with configurational entropy of the polymer (Sukeshini et al 1996 and Ramesh et al 2000).
The ionic conductivity in polymer electrolyte is assumed to occur by Lewis acid base interaction between salt and polymer solvent (Croce et al 1998, Krawiec et al 1995 and Christie et al 2005). Chitin, chitosan and hydroxy apatite nanofillers contain polar OH group on the surface. The polar anions dissociate from the salt, transiently H-bonded to the OH group and the migration will be facilitated. It also has basic groups like NH$_2$ in the case of chitosan, NH-COCH$_3$ for chitin and PO$_4^{3-}$ for nHAp. These basic groups can interact with Li$^+$ cations by forming transient links (co-ordinate/dative bond) to facilitate Li$^+$ ion migration. This is also seen as an increase in the average mobility of charge carriers. The schematic illustrations of ionic conduction mechanism in polymer electrolytes and NCPEs are shown in scheme 4.1 and 4.2 respectively.

![Scheme 4.1 Ionic transport between PEO and Li salt](image-url)
Scheme 4.2 Expected ionic transport mechanism between PEO, Li salt and nanofillers (when R=H/ NC or R= COCH₃/CNF)

The ionic conductivity as a function of temperature for various compositions of nanofillers (NC/CNF/nHAp) incorporated polymer electrolytes is shown in Figures 4.11, 4.12 and 4.13 respectively.

It is observed from the Figures (4.11-4.13), that ionic conductivity increases with increase in concentration of nanofillers up to 10 wt %. The increase in ionic conductivity is due to the availability of conducting ions in the polymer matrix. These results are in accordance with earlier reports in which Al₂O₃ was used as filler in PEO based electrolyte (Wieczoreck et al 1996). The Lewis acid base reactions between filler surface and the PEO segments may induce structural modifications in the polymer matrix (Wieczoreck et al 1989). Also the nanofillers (NC/CNF/nHAp) can act as cross linking centers for the PEO segments, which lower the polymer chain
reorganizing tendency and promoting an overall stiffness to the structure. However, the resulting structure provides Li\(^+\) ion conducting pathways at the filler surface and enhances ionic transport. The conductivity decreases gradually when the concentration of filler increases beyond 10 wt\%. This is due to phase discontinuities and the dilution effect predominates which led to low ionic conductivity. The drop in conductivity may be attributed to an aggregation of nanoparticulates that can strongly interact with the polymer chains by immobilizing them in the process.

![Graph showing ionic conductivity as a function of temperature for NC incorporated NCPEs]

**Figure 4.11** The ionic conductivity as a function of temperature for NC incorporated NCPEs
Figure 4.12 The ionic conductivity as a function of temperature for CNF incorporated NCPEs

Figure 4.13 The ionic conductivity as a function of temperature for nHAp incorporated NCPEs
Similarly, the conductivity increases with increase in salt content up to 5 wt% as shown in Figure 4.14. When more lithium salt is added, the conductivity slowly decreases. This may due to the formation of neutral ion pairs which reduce the density of mobile ions (Johan et al 2010). The slow increase in conductivity at lower concentration implies that the number of mobile ions increases proportionally with amount of lithium salt up to a certain wt%.

![Figure 4.14 Ionic conductivity as a function of temperature for polymer-lithium complexes PEO_{100-X} Li_x (X=1, 3, 5 and 7)](image)

Among the three types of nanofillers (NC/CNF/nHAp) incorporated polymer electrolytes, NC incorporated polymer electrolytes yield maximum ionic conductivity and rise to the order of 10^{-3} S/cm. This may due to easy formation of dative bond with polymer compared to other two fillers. The increasing order of ionic conductivity of various nanofillers (NC/CNF/nHAp) incorporated polymer electrolytes are given below.
NC incorporated PE (NC2) (10^{-3} S/cm) > CNF incorporated PE (CNF2) (10^{-3.2} S/cm) > nHAp incorporated PE (HA2) (10^{-3.4} S/cm).

4.1.6 Dielectric analysis

Study of the dielectric process of a material is an important tool for valuable information about conduction process. The dielectric property indicates the amount of charge that can be stored by a material and it can be used as an indicator to prove that, the increase in ionic conductivity is due to increase in charge carriers. A wide frequency range dielectric relaxation spectroscopy is an essential tool to study the relaxation of dipoles in polymer electrolytes.

The complex permittivity (\(\varepsilon^*\)) or dielectric constant of a system is evaluated by means of following expression (Equation 4.4),

\[
\varepsilon^* = \varepsilon' - j\varepsilon''
\]  \hspace{1cm} (4.4)

where \(\varepsilon'\) is the real part of dielectric constant and \(\varepsilon''\) is the imaginary part of dielectric constant of the material

\[i.e.\quad \varepsilon' = \frac{\varepsilon C}{\varepsilon_0 A} \]  \hspace{1cm} (4.5)

\[\varepsilon'' = \frac{\sigma'}{\omega \varepsilon_0} \]  \hspace{1cm} (4.6)

where \(\sigma'\) is the real part of conductivity (in S/cm), \(C\) is the parallel capacitance (in F), \(d\) (in cm) and \(A\) (in cm²) are thickness and area of the polymer electrolyte in contact with the electrode respectively. \(\omega\) is the angular frequency and \(\varepsilon_0\) is the permittivity of free space (8.856x 10^{-14} F/cm). The variation of \(\varepsilon'\) with frequency for NC, CNF and nHAp incorporated NCPEs are presented in Figures 4.15, 4.16 and 4.17 respectively. The response shown in the figures were restricted to the samples NC2, CNF2 and HA2. The
reason for choosing these samples is due to the fact that they exhibited high ionic conductivity at room temperature compared to other prepared electrolytes. It is observed from the Figures 4.15-4.17, that $\varepsilon'$ decreases with increasing frequencies for all the three NCPEs prepared by incorporating various nanofillers (NC/CNF/nHAp). This is due to the reason that, space charge region builds up at the electrode and electrolyte interface (Armstrong et al 1974 and Armstrong et al 1973). At low frequency region, the permanent dipoles align themselves along the direction of the applied field and contribute to the total polarization of the dielectric material. Moreover, higher the frequency, the variation of field is too rapid for the dipoles to align themselves in the direction of field. \textit{i.e.}, the dipoles can to longer follow the field direction and hence to the $\varepsilon'$ become negligible. Therefore, the dielectric constant decreases with increase of frequency.

![Figure 4.15](image)

\textbf{Figure 4.15} The variation of $\varepsilon'$ as a function of frequency for NC2 at different temperatures
Figure 4.16  The variation of $\varepsilon'$ as a function of frequency for CNF2 at different temperatures

Figure 4.17  The variation of $\varepsilon'$ as a function of frequency for HA2 at different temperatures
Figures 4.18, 4.19 and 4.20 show the variation of imaginary part of permittivity as a function of frequency. In the present system, the conduction losses dominate at lower frequencies and hence at all temperatures the dielectric loss ($\varepsilon''$) shows $1/\omega$ dependence of frequency. It is also found that the dielectric loss increases with increase in temperature. The relationship between conductivity and the dielectric loss factor is given by following expression (Equation 4.7)

$$\varepsilon'' = \sigma/\omega C_0$$

(4.7)

Since $\sigma$ is strongly dependent on temperature, the dielectric loss also depends on temperature and hence increase in $\varepsilon''$ value of NCPEs with increase of temperature.

Figure 4.18  The variation of $\varepsilon''$ as a function of frequency for NC2 at different temperatures
Figure 4.19  The variation of $\varepsilon''$ as a function of frequency for CNF2 at different temperatures

Figure 4.20  The variation of $\varepsilon''$ as a function of frequency for HA2 at different temperatures
4.1.7 Electric modulus analysis

Complex modulus electric spectra analysis is used to examine the electric response of NCPEs. The conductivity behavior in the frequency domain range is interpreted in terms of following equations (Equations 4.8-4.10).

\[ M'(\omega) = \frac{1}{\varepsilon'_\omega} \]  
\[ M''(\omega) = \omega C_0 Z'(\omega) \]  

(4.8)  
(4.9)

The complex modulus \( M'(\omega) \) is the sum of real part of electric modulus and imaginary part of electric modulus

\[ M'(\omega) = M'(\omega) + jM''(\omega) \]  

(4.10)

where \( C_0 \) is the vacuum capacitance of the cell and \( \varepsilon'_\omega \) is the complex permittivity and \( j = \sqrt{-1} \) respectively.

The variation of \( M' \) and \( M'' \) with frequency for NC, CNF and nHAp incorporated NCPEs are presented in Figures 4.21-4.26. The response in the figures was restricted to the samples NC2, CNF2 and HA2. The reason for choosing these samples are due to the fact that it yields high ionic conductivity at room temperature compared to other electrolytes prepared in the study. As the temperature increases, the values of \( M' \) and \( M'' \) have decreased gradually due to plurality of relaxation mechanism (Ramesh et al 2001 and Mishra et al 1998). From the figures, it is noted that the \( M' \) and \( M'' \) values increase only in the higher frequency region. The values of \( M' \) and \( M'' \) tend to be zero in the vicinity at lower frequencies which proposes that the electrode polarization at interface is negligible at lower frequencies. Only in the rising portion of the \( M' \) and \( M'' \) values, the frequency dispersion is
observable (Figures 4.21-4.26). The zero value of M' and M" at lower frequencies indicates the negligible electrode polarization for the system. The presence of long straight line in the low frequency region confirms a large equivalent capacitance (pF) associated with electrode interface. The presence of peak in the M" formalism (Figures 4.21-4.26) at higher frequency for NCPEs indicates that ionic conduction is predominant in the polymer electrolyte systems. As the temperature increases, the M" maximum shifts to higher frequencies which indicate that the conductivity of the charge carrier has been thermally activated. These outcomes are in accordance with the results reported earlier (Nadkarni et al 1970 and Selvasekarapandian et al 2003).

![Figure 4.21](image)

**Figure 4.21** The variation of M' as a function of frequency for NC2 at different temperatures
Figure 4.22  The variation of $M'$ as a function of frequency for CNF2 at different temperatures

Figure 4.23  The variation of $M'$ as a function of frequency for HA2 at different temperatures
Figure 4.24 The variation of $M''$ as a function of frequency for NC2 at different temperatures

Figure 4.25 The variation of $M''$ as a function of frequency for CNF2 at different temperatures
Figure 4.26  The variation of $M''$ as a function of frequency for HA2 at different temperatures

4.1.8  Electrochemical Studies

Cyclic voltammetry (CV) studies have been carried out to confirm the reversible nature of polymer electrolytes. CV studies were carried out using a symmetric Li/NCPE/Li cell fabricated in our lab. The interest is on the determination of electrochemical stability of PEO based polymer systems and the effect of nanofillers (NC/CNF/nHAp) upon this stability.

The cyclic voltammogram of various nanofillers (NC/CNF/nHAp) incorporated NCPEs are depicted in Figures 4.27-4.29.
Figure 4.27 The cyclic voltammogram of PE1 and NC2

In all the cases, the samples PE1 (without filler) and NC2, CNF2 and HA2 were subjected to CV studies at a scan rate of 10 mV/s. The purpose of choosing NCPEs NC2, CNF2 and HA2 is due to the fact that it yielded high room temperature ionic conductivity. It is observed from the Figure 4.27, that the cathodic deposition and anodic stripping of Li⁺ ion are facile at the Li/NCPE interface. *i.e.* when the potential is less than 0 V, deposition of Li⁺ ion takes place thereby increasing the anodic peak current. In a similar manner, the stripping of Li caused significant increase of cathodic peak current when the potential exceeds 0 V. It is important to note that the incorporation of nanofillers (NC/CNF/nHAp) progressively decreases the peak potential difference between lithium stripping and deposition. The potential difference in the case of sample PE1 was 1.5 V whereas in nanofiller incorporated NCPE NC2, it has found to be 1.01 V.
Figure 4.28 The cyclic voltammogram of PE1 and CNF2

The incorporation of nanofillers (NC/CNF/nHAp) also significantly increases the peak current compared to that of PE1 which may due to effective ionic transport at grain boundaries of Li$_2$O rather than LiF. The observation of both anodic stripping and cathodic deposition in CV studies confirms the movement of Li ions in the polymer matrix. Similar types of results were reported earlier for other systems (Croce et al 1991, Park et al 2006 and Nookala et al 2002).
Figure 4.29 The cyclic voltammogram of PE1 and HA2

4.1.9 Interfacial studies

As compared to carbon-based anode, lithium metal is found to be attractive anode material for secondary rechargeable lithium batteries due to its high specific capacity. The interfacial properties of lithium metal anodes with composite polymer electrolyte play a major role which includes shelf life, safety, lithium deposition and dissolution efficiency and cyclic life (Manuel Stephan et al 2006).

The effect of nanofillers (NC/CNF/nHAp) in the interfacial properties with lithium metal anode was studied. The Li/NCPE/Li symmetric cells were fabricated and studied at 60 °C. In all the cases, the samples NC2, CNF2 and HA2 are particularly chosen as this composition yielded maximum ionic conductivity among the NCPEs prepared in the present study. The
variation of interfacial resistance as a function of time for NCPE containing lithium salt LiTf and nanofillers (NC/CNF/nHAp) is shown in Figures 4.30-4.32. It exhibits that, NC incorporated polymer electrolyte, NC2 possess better interfacial properties than PE1. *i.e.* the interfacial resistance $R_i$ decreases gradually for NC2 as compared to PE1. But the sudden rise in $R_i$ may be due to two factors:

1. Due to the reaction of polymer electrolyte and nanochitosan with lithium electrode, the high resistance passivation films such as Li$_2$O and LiF may have formed which had caused dendritic growth and cell shorting on lithium surface.

2. Further the lithium metal anode also reacts with protic and aprotic solvent. Thus the growth of $R_i$ did not follow a regular manner for NCPEs NC2.

![Graph showing the variation of interfacial resistance as a function of time for PE1 and NC2](image)

*Figure 4.30  The variation of interfacial resistance as a function of time for PE1 and NC2*
In the case of CNF2, the value of interfacial resistance $R_i$ has been reduced by the incorporation of CNF as compared to filler free electrolyte PE1. Moreover the value of $R_i$ does not follow a uniform manner. *i.e.*, it decreases slowly with time and then increases. The sudden increase in $R_i$ at 72 hrs may due to reaction of lithium metal anode with polymer electrolyte. The $R_i$ value of HA2 decreases gradually for first 72 hrs and after 144 hrs, it increases rapidly due to formation of additional layer over the lithium electrode and does not follow uniform pattern (*i.e.*, initially, it decreases with increase in time afterwards it slightly increases. After 180 hrs, the resistance values did not change much. This may be due to the reason that the morphology of passivated film changes with time to acquire a non compact porous structure. The immediate rise in $R_i$ may be due to the above said two factors as mentioned in the case of NC2.

![Graph](image)

**Figure 4.31** The variation of interfacial resistance as a function of time for PE1 and CNF2
Figure 4.32  The variation of interfacial resistance as a function of time for PE1 and HA2