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Effect of Nanochitosan on Structural, Thermal and Electrochemical Properties of Poly Ether Based Polymer Electrolytes Complexed with Lithium Bis(Trifluoromethanesulfonyl Imide)

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Abstract: *In this research, nanocomposite membranes were prepared using polyethylene oxide as polymer host, lithium bis(trifluoromethanesulfonyl imide) as salt and nanochitosan as inert filler. Initially nanochitosan was prepared from chitosan by ionotropic gelation method. Nanocomposite membranes were prepared by solvent free membrane hot press technique. The prepared membranes possessed excellent physico-chemical properties. The complexing behavior and structural reorganization in polymer electrolytes were analyzed by XRD and FT-IR analyzes. The decrease in crystalline nature of polymer electrolytes was confirmed by DSC analysis. The electrolyte S3 possessed high conductivity and attained a maximum of* $10^{-3.01}$ *S/cm.*

Keywords: nanochitosan, nanocomposite electrolytes, ac ionic conductivity, dielectric analysis

1. INTRODUCTION

In recent times, in the area of active research and development, composite solid polymer electrolytes (CSPE) received much attention due to their wide potential applications in rechargeable lithium polymer batteries and electrochemical super capacitors [1-3]. Among various polymer electrolytes, CSPE is of quite interest because it possesses several advantages such as wide operating temperature, longer shelf-life, easy handling, good interfacial contact and no internal shorting. A major quantity of research has done in this aspect in order to optimize the properties of polymer electrolytes and its applicability to lithium batteries for last two decades. Polyethylene oxide (PEO) seems to be a promising candidate in the search of polymer electrolytes owing to its high thermal and interfacial stability. However, the high degree of crystallinity of PEO offers very low ionic conductivity at ambient temperatures when complexed with lithium or other alkaline salts and it yields high ionic conductivity only above its crystalline temperature (T_m). To improve the ionic conductivity of CSPE at ambient temperature various methods are evolved such as incorporating filler, addition of plasticizer or blending other suitable polymers, which will increase the amorphous region thereby increasing the ionic conductivity. Lithium bistrifluoromethanesulfonylimide (LiTFSI) plays a vital role as doping salt owing to non- toxic, resistant to oxidation, thermally stable and less hygroscopic nature. In the present work, biopolymer nanochitosan (NC) is used as inert filler. It exhibits several interesting properties such as biocompatibility, biodegradability, antimicrobial, non-toxic and non-allergenic nature. It finds applications in medical, pharmaceutical, controlled drug delivery system, food industry, paper finishing and solid state batteries. The incorporation of NC in polymer matrix significantly enhances the mechanical and conducting nature of polymer electrolyte film and the conductivity is in the order of 10^{-3} S/cm which was reported earlier by us using lithium triflate as salt [4]. In the present study,

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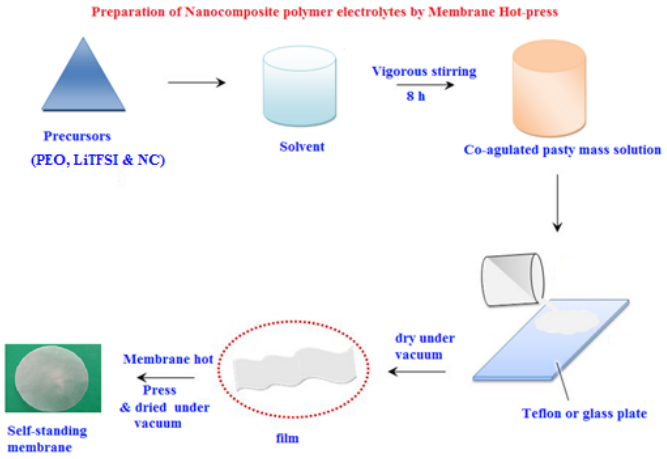
Scheme 1. Preparation route of NCSPEs by hot-press method



we have planned to investigate the effect of NC in PEO matrix complexed with LiTFSI in order to obtain better ionic conductivity than the previous one leading to solid-state lithium battery application. To the best of our knowledge the effect of NC in PEO-LiTFSI nanocomposite solid polymer electrolyte (NCSPE) have never been investigated. The details are presented herein.

2. EXPERIMENTAL

2.1. Preparation of NCSPEs

The synthesis and characterization of NC was reported already in the previous work [4]. All the precursor materials were dried under vacuum for 48 h at 50 °C before use. NCSPE consisted of polymer PEO with molecular weight (M_w) of 2×10^5 (Sigma Aldrich), LiTFSI (Merck) as salt and synthesized NC as inert filler were prepared by membrane hot-press method as described elsewhere [5, 6]. The weight content of polymer and lithium salt was maintained at 8.5:1 which indicated that there was sufficient number of available sites (O-atom in PEO) for lithium ion to hop from one site to another site. In the present investigation, the optimized wt % of lithium salt was 5, which were inferred from trial and error method [4]. The various compositions of precursor materials PEO, LiTFSI and NC are tabulated in table 1.

The hot-pressed membranes were dried under vacuum at 50 °C for 48 h for further removal of solvent present in the membrane. The resulting membranes were usually examined for its dryness and freestanding nature. The synthetic scheme of nanocomposite solid polymer electrolytes (NCSPEs) is shown in scheme 1.

Table 1. Various compositions of PEO, LiTFSI and NC

Sample code	PEO (Wt%)	LiTFSI (Wt%)	NC (Wt%)
S1	95	5	-
S2	92	5	5
S3	85	5	10
S4	85	7	8
S5	80	5	15

2.2. Instrumentation

The prepared electrolytes were subjected to various physico-chemical characterizations. Here, the amorphous degree of nanocomposite polymer electrolytes was investigated using BRUKER AXSD8 advanced X-ray diffractometer with CuKα radiation (λ=1.5412 Å). The accelerating voltage was set at 40 kV with 30 mA fluxes at a scanning rate of 20°/m in the 2θ range between 10 and 80°.

The infrared spectra of NCSPEs were carried out by using FT-IR spectrometer (JASCO FT-IR L4100, Japan) spectrum with ATR, an internal reflection accessory in the wavenumber region between 4000 cm^{-1} and 400 cm^{-1}. The resolution of the spectra obtained at room temperature was 2 cm^{-1} and recorded in the transmittance mode.

DSC analysis was carried out to determine the thermal behavior of NCSPEs in the temperature range 20 – 100 °C at a heating scan rate of 10 °C/min in nitrogen atmosphere using SDT. Samples were hermetically sealed in an aluminum pan and perforated in order to keep the samples at atmospheric pressure. The temperature was then maintained at 70 ^oC for 2 minutes to ensure the complete evaporation at a heating rate of 10 ^oC/min. The final heating scan was used to evaluate the T_m. The endothermic peak of melting was assigned as T_m.

The ionic conductivity was measured using electrochemical impedance analyzer (ZAHNER, IM6, Electrochemical work station, Germany) connected to a computer for data acquisition. The thickness of the NCSPEs was measured by using a micrometer screw gauge. The parameter of thickness of the NCSPEs was very vital because the result might affect if there was any change of thickness. The measurement of thickness should be repeated a few more times on to the surroundings of the samples in order to obtain an average thickness. It aimed to produce more precise results. The NCSPEs were sandwiched between two gold blocking electrodes in the frequency range between 100 mHz and 100 kHz with a signal amplitude of 1 V at 16 points frequency per decade. Ionic conductivity was calculated from the impedance response using a widely accepted equivalent circuit model and extracting the bulk resistance of the electrolyte from the higher frequency response.

The temperature dependence ionic conductivity study of NCSPEs samples were measured in the temperature range 30 and 70 °C. The bulk resistance of NCPE and PNCPE was determined by using the following equation

$$\sigma = \frac{t}{R_b A} \quad (1)$$

where, t is the thickness (cm); R_b is the bulk resistance (Ω) and A is the known surface area (cm^2) of NCSPEs. The semicircle fitting was accomplished to obtain R_b value. R_b of the thin electrolyte films were calculated from extrapolation of the semicircular region on Z real axis (Z'). Besides, Z' and Z" axes must be in equal scale because the radius of a circle must be the same.

3. RESULTS AND DISCUSSIONS

3.1. X-ray Diffraction Analysis of NCSPEs

The X-Ray diffraction studies were carried out to confirm the formation of the composite material and its phase identification.

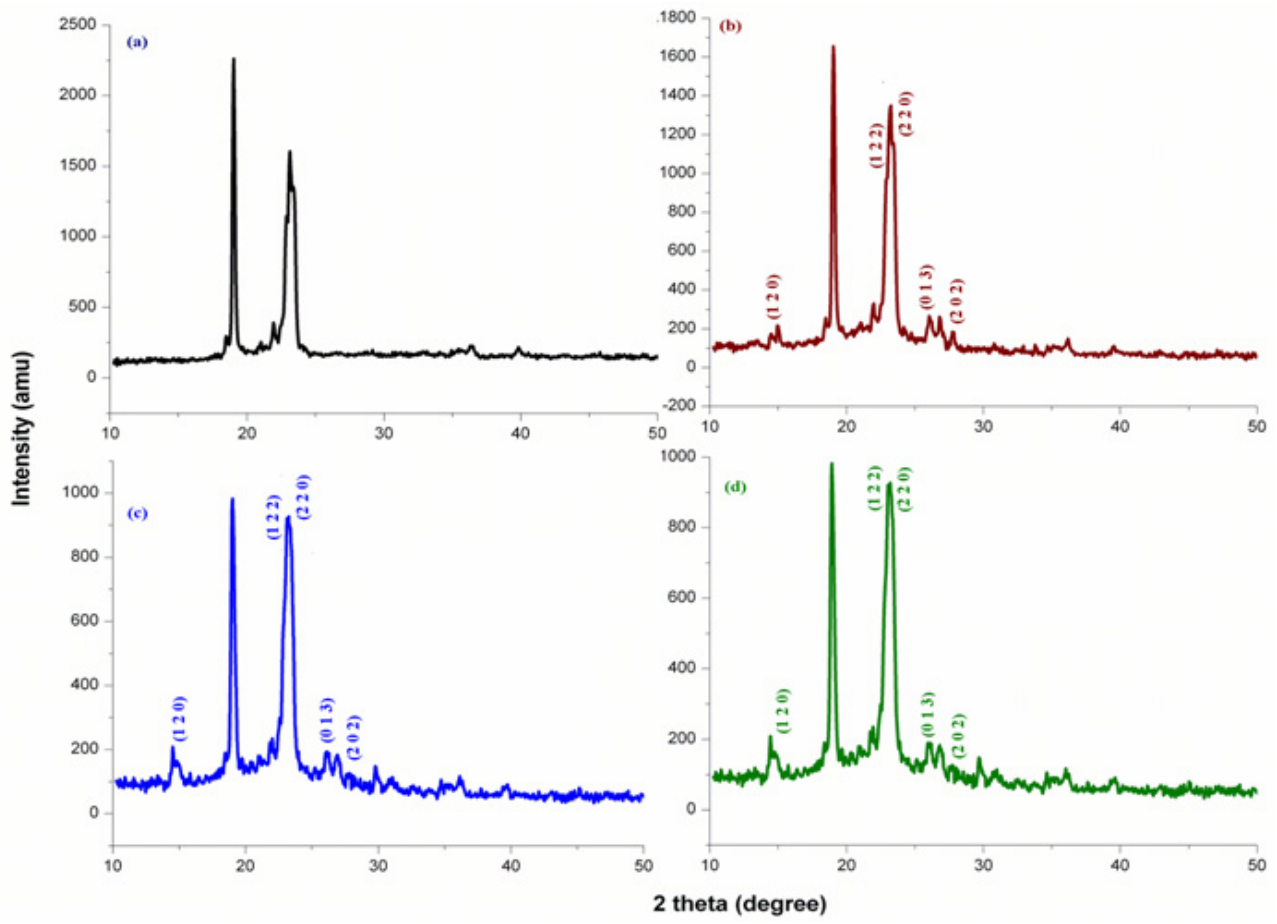


Figure 1. (a-d). The XRD patterns of S1 (without NC) and NCSPE's S2, S3 and S4

The accurate determination of inter-planar spacing, crystallinity and various micro-structural parameters etc. from XRD pattern also provides an important basis in understanding the various physical properties of the polymeric materials. The XRD patterns of S1 (without NC) and NCSPE's S2, S3 and S4 are depicted in Fig.1 (a-d). The XRD patterns of S1 showed the presence of few crystalline peaks and amorphous humps indicating the semi-crystalline nature of the polymer electrolyte. The XRD patterns of pure PEO consists of two main peaks appearing around 2θ = 19° and 23° [5]. The XRD patterns of polymer salt complexes are analogous to that of the host PEO [7] indicating the complexation of polymer with salt. Also, the peaks for LiTFSI is absent in all the diffractograms, which show that the added salt is completely dissolved in the polymer matrix [7]. The diffractions peaks at 15.19° and 23.12° correspond to the (120) and (220) reflections of chitosan. In figures1 (b) to 1(d), it is observed that the intensity of the crystalline peaks was decreased and broadened upon the addition of nanochitosan. However, the peaks corresponding to chitosan remains unaltered. This observation shows that the polymer undergoes significant structural reorganization due to the addition of filler and lithium salt. Also, due to the addition of filler there is a reduction in the crystallinity of the polymer, which changes the reorganization of the polymer chains. The peak observed around 19° shifts towards the low angle side with increase in NC ratio.

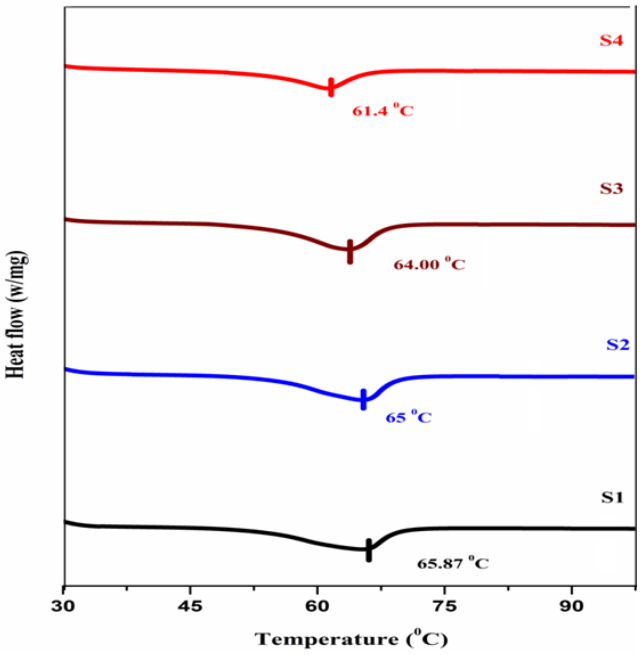


Figure 2. (a-e). DSC thermograms of samples S1-S4

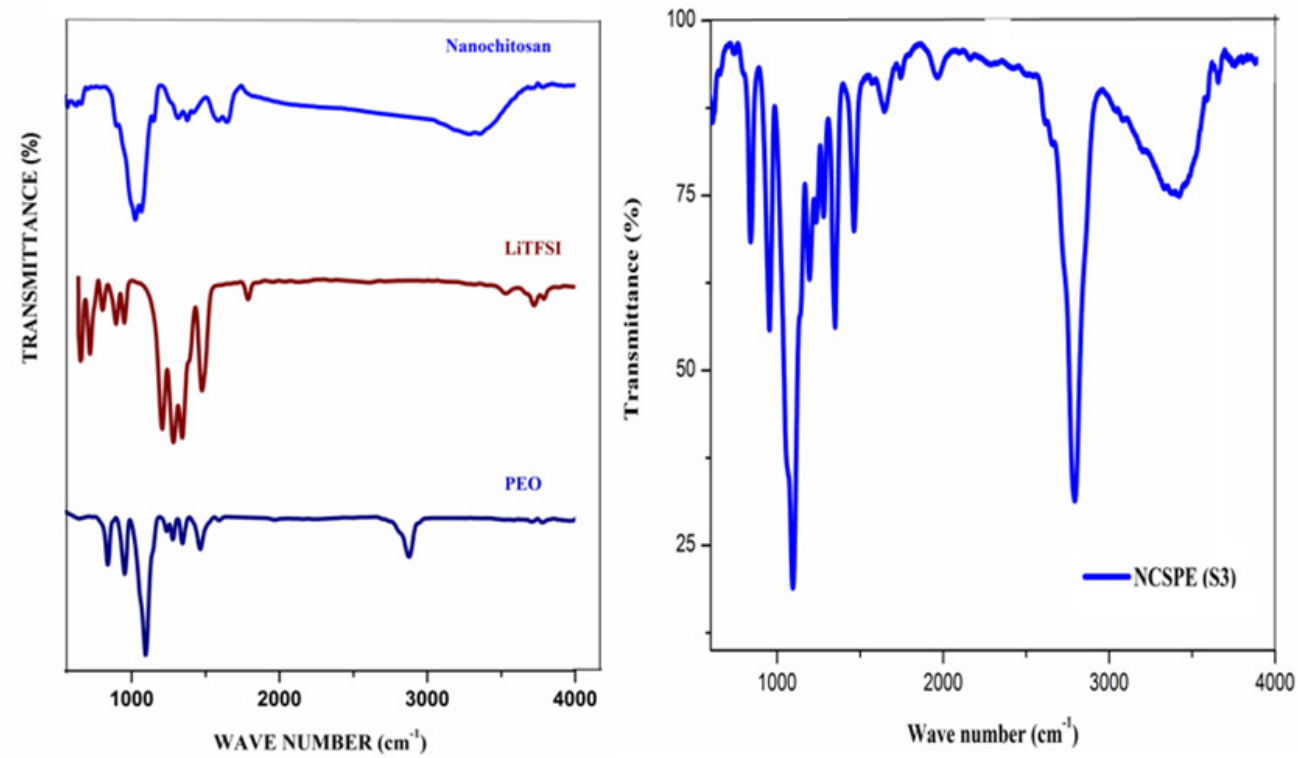


Figure 3. (a-d). FTIR spectra of PEO, S1, NC and S3

3.2. Differential Scanning Calorimetry Analysis (DSC) of NCSPEs

DSC thermograms of samples S1-S4 were recorded from 20 to 100 °C and are shown in Fig. 2 (a-d). The incorporation of NC and LiTFSI into the polymer matrix results in the broadening of the melting endothermic peak with an apparent decrease in the heat of enthalpy (ΔH_m). The percentage crystallinity of PEO based NCPEs has been determined from the following empirical equation,

$$\%\alpha = \left({}^{\Delta H_m}/_{\Delta H_{m100\%}}\right) \times 100 \quad (2)$$

$\Delta H_{m100\%}$ represents the heat of enthalpy of pure PEO. The value of $\Delta H_{m100\%}$ for PEO is 213.7 J/g [8]. The value of ΔH_m is calculated from the area under the melting peak of DSC curve. The values of T_m and percentage of crystallinity (% α) of S1, S2, S3 and S4 are summarized in Table 2. The value of crystallinity as well as ΔH_m is found to decrease significantly in the presence of filler in the polymer matrix. The reduction in value of crystallinity and melting temperature is due to the fact that the addition of LiTFSI and NC enhances segmental motion and flexibility of PEO host polymer matrix. This observation confirms that the addition of LiTFSI and NC diminishes the crystalline nature of polymer as well as enhances the amorphous nature of polymer, thereby increasing the ionic conductivity. Both XRD and DSC results confirm that PEO crystallinity has been hindered by the large anion of LiTFSI and also by the incorporation of NC. Similar behavior is exhibited for other polymer electrolytes, which have been reported earlier [9].

3.3. FT-IR spectra of NCSPEs

FTIR spectroscopy is important for the investigation of polymer structure. Since, it provides information about the complexation and interactions between the various constituents in the polymer electrolyte. These interactions can induce changes in the vibrational modes of the molecules in the polymer electrolyte. The FTIR spectra of PEO, S1, NC and 85%PEO+5%LiTFSI+ 10 wt % NC are shown in figure 3. The peaks (fig. 3a) that appear at 2888 and 2740 cm^{-1} in pure PEO correspond to symmetrical and asymmetrical stretching modes of CH_2−group respectively. Moreover, the peaks appearing at 1260, 1240 and 1155 cm^{-1} are assigned to asymmetric CH_2-twisting, symmetric CH_2-twisting modes and C–O–C asymmetric stretching mode of pure PEO respectively. The addition of LiTFSI in the polymer matrix could be identified by the peaks that appear at 798 and 770 cm^{-1} which corresponds to C-S and S-N-S stretching. Moreover the characteristic peaks at 740, 648, 598 cm^{-1} correspond to δ_s of CF_3, $\delta_{S\text{-}N\text{-}S}$ and δ_a SO_2 respectively. The shifting

Table 2. Values of T_m and percentage of crystallinity (% α) of S1, S2, S3 and S4

Sample code	T_m (°C)	% α
S1	65.87	86.10
S2	65.00	68.00
S3	64.00	66.54
S4	61.40	62.11

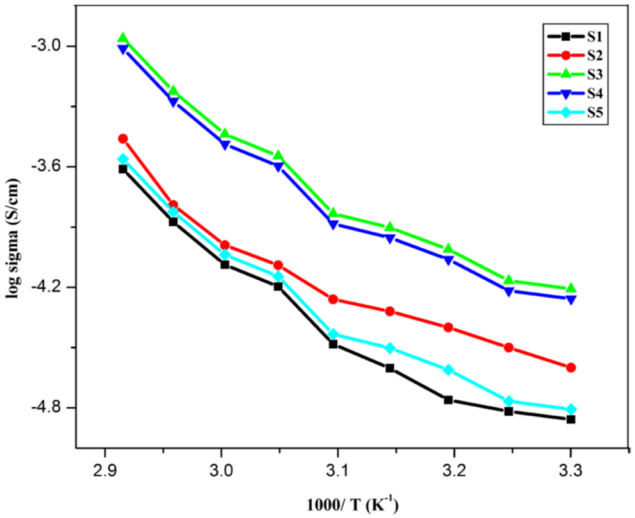


Figure 4. Variation of ionic conductivity as a function of reciprocal of temperature for various nanocomposite solid polymer electrolytes (S1 to S5).

of peaks in the region from 1144 to 1090 cm^{-1} indicates that the addition of lithium salt made appropriate change in the polymer matrix which is shown in fig. 3c. Furthermore, the shifting of peak from 953 cm^{-1} (pure PEO) to 951 cm^{-1} (PEO + lithium salt) indicates the complexation behavior of the polymer electrolyte. The characteristic peaks that appear at 889, 1582, 1360–1020 and 3739 cm^{-1} correspond to polysaccharide, N–H stretching, C–N stretching and O–H group of nanochitosan respectively. The presence of nanochitosan in the polymer electrolyte is confirmed from the shifting of peaks from 889 to 839, 1360 to 1351 and 3739 to 3733 cm^{-1} (Fig. 3d).The above analysis establishes the formation of the polymer–salt–filler complex.

3.4. Electrochemical properties of NCPEs

a) Ionic conductivity of NCPEs

The variation of logarithm of ionic conductivity as a function of inversion temperature for different wt% of NC based NCSPE's are depict in Fig. 4. As it is evident from the figure that the ionic conductivity of NCPE's obeys Vogel-Tamman-Fulcher relation [VTF] (eqn.3) i.e., the conductivity increases with increase in temperature.

$$\sigma = \frac{A}{T^{1/2}} e^{-B/T-T_g} \quad (3)$$

where, A and B are constants. The constants A and B in VTF equation are related to the number of charge carriers and activation energy of ion transport associated with configurational entropy of polymer respectively [10]. It is also noticed from figure 4, that the conductivity increases with increase in NC content up to 10 wt%. This is due to the fact that the NC increases the polymer chain segmental motion as well as the amorphous region. These amorphous regions favor the movement of lithium ion in the free volume of polymer matrix. The conductivity of NC incorporated PEO based polymer electrolytes increases one order of magnitude compared to filler free electrolyte S1. In the mean time, the incorporation of NC increases beyond 10 wt%, the sudden decrease in ionic conductivity observed is due to phase discontinuities and dilution effect predominates in the polymer matrix. Also, the addition of lithium salt (LiTFSI) in the polymer is optimized and the optimized wt% is 5. When the concentration of LiTFSI exceeds 5 wt%, the sample with anion $[(CF_3SO_2)_2]_2$ forms neutral ion pairs with cation which leads to the decrease of available number of free moving ions (charge carriers) in the polymer matrix. The maximum ionic conductivity is found to be in the range of $10^{-3.01}$ S/cm for polymer electrolyte S3 (10 wt% NC).

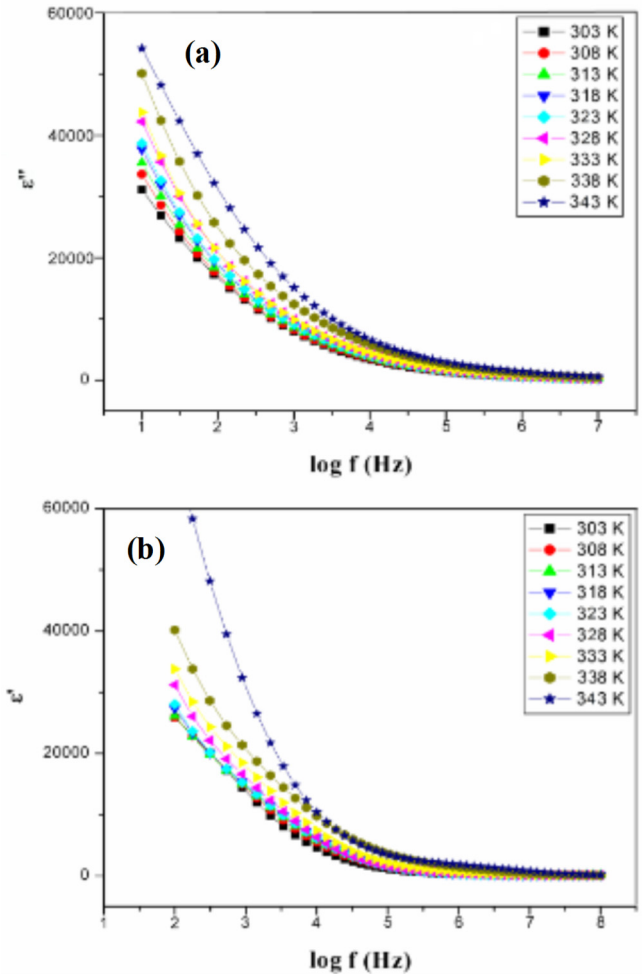


Figure 5. (a-b). Frequency dependence of (a) real part ε' (ω) and (b) imaginary part ε''(ω) of dielectric permittivity for S3 at different temperatures.

b) Dielectric Properties of NCPEs

A wide frequency range of dielectric relaxation spectroscopy is an essential tool to study the relaxation of dipole in plasticized polymer electrolytes. The complex permittivity ε* or dielectric constant of a system was evaluated by means of the following expression,

$$\varepsilon * = \varepsilon' - j\varepsilon'' \quad (4)$$

Where, ε' is the real part of the dielectric constant and ε" is the imaginary part of the dielectric constant of the material

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A} \quad (5)$$

i.e.

$$\varepsilon'' = \frac{\sigma'}{\omega \varepsilon_0} \quad (6)$$

where, σ' is the real part of the conductivity (S/cm), C is the parallel capacitance (F); d (cm) and A (cm^2) are thickness and area of the polymer electrolyte respectively, ω the angular frequency and ε_o is the permittivity of free space which is equal to 8.856×10^{-14} F/cm.

The variation of ε' and ε" as a function of log frequency for sample S3 at different temperatures is shown in Fig. 5(a & b). It is observed from the figure that ε' and ε" decreases with increase in frequencies. This is due to the reason that, space charge region builds up at the electrode and electrolyte interface which is also known as non-Debye type of behavior. The dependence of frequency with space charge region is elucidated in terms of ion diffusion. When the frequency is low, the values of ε' and ε" become large which is due to the increase of charge carrier density at the space accumulation region (or the number of free moving ions in the electrolyte). This results in an increase in equivalent capacitance (lies in the range of pico-Farad (pF)) at the electrolyte interface. At high frequencies, high periodic reversal of field takes place as well as the available number of free moving ion decreases at electrolyte interface, so ε' and ε" decreases gradually [11,12]. In the intervening time the value of ε' and ε" have increased step by step at higher temperature due to the available number of free moving ions/charge carriers increase at high temperatures. These observations suggests that the polarization due to charge carrier density at space accumulation region is directly proportional to the value of ε' and ε".

c) Electric modulus analysis

The complex modulus electric spectra analysis is used to examine the electric response of NCPE. The conductivity behavior in the frequency domain range is interpreted in terms of the following representations.

$$M'(\omega) = \frac{1}{\varepsilon^* \omega} \quad (7)$$

$$M''(\omega) = \omega C_0 Z^*(\omega) \quad (8)$$

The complex modulus M*(ω) is the sum of the real part of electric modulus and imaginary part of electric modulus

$$M*(\omega) = M'(\omega) + jM''(\omega) \quad (9)$$

i.e.,

where, C_o is the vacuum capacitance of the cell and ε' (ω) is the complex permittivity and j=√-1 respectively.

Figure 6 (a & b) shows the frequency dependence of M' and M" for sample S3 at different temperatures. From the figure, it is observed that at high frequencies the value of M' and M" attains maximum, but, well defined peaks are not obtained. As the temperature increases, the peaks of M' and M" have decrease gradually due to the plurality of relaxation mechanism. The value of M' and M" tends to be zero in the vicinity at lower frequencies which proposes that the electrode polarization at the interface is negligible at lower frequencies. The presence of long straight line in the low frequency region confirms a large equivalent capacitance associated with electrode interface [13]. In the mean time the value of M' and M" decreased slowly at higher temperatures due to the decrease in charge carrier density at the space accumulation region. These outcomes are in accordance with the results reported in the literature earlier [14].

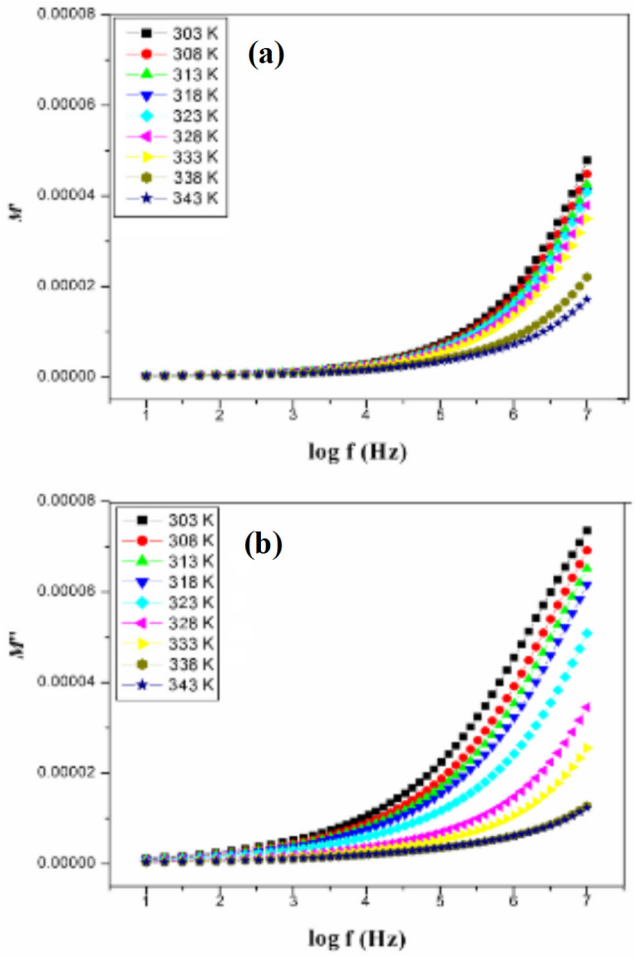


Figure 6. (a-b). Frequency dependence of (a) real part *M*' (ω) and (b) imaginary part *M*" (ω) of electric modulus for S3 at different temperatures.

4. CONCLUSIONS

Various series of PEO based polymer nanocomposite electrolytes containing $LiN((CF_3SO_2)_2)$ as salt and NC as nanofiller were prepared by hot-press technique and then subjected to various structural, thermal, electrical and electrochemical characterizations. The maximum ionic conductivity was found to be in the order of $10^{-3.01}$ S/cm for 10 Wt% NC. The ion-polymer –filler interactions were confirmed by FT-IR analysis. The decrease in polymer host matrix was confirmed by XRD and DSC analyses.

5. ACKNOWLEDGEMENTS

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