Dielectric relaxation spectroscopy and ion conduction in poly(ethylene oxide)-blend salts-montmorillonite nanocomposite electrolytes

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Poly(ethylene oxide) (PEO) and blend alkaline metal salts (equal number of cations of lithium perchlorate trihydrate and sodium perchlorate monohydrate) complexations with montmorillonite (MMT) nanoclay filler up to 20 wt% concentration were synthesized by direct melt compounded hot-press technique at temperature 104°C under 3 tons pressure. The spectra of complex dielectric function, electric modulus, and alternating current (ac) electrical conductivity and complex impedance plane plots of these polymer nanocomposite electrolytes were investigated in the frequency range 20 Hz - 1 MHz at ambient temperature. Relaxation times corresponding to electrode polarization and ionic conduction relaxation processes, and their correlation with dc ionic conductivity were explored. It has been recognized that the increase of MMT concentration results in stiffening of the PEO–MMT transient cross-linked structures, which decreases the PEO chain segmental dynamics and the cations translational motion.

Keywords: Polymer nanocomposite electrolytes, Dielectric relaxation, Ionic conductivity

1 Introduction

In recent years, there has been an increasing interest to develop flexible solid-type polymer nanocomposite electrolytes (PNCEs) of improved mechanical, thermal and electrochemical properties for their potential applications in electrochemical display devices, capacitors, portable power sources, fuel cells, sensors, solar cells, etc.1-12 It has been established that the addition of a small amount of montmorillonite (MMT) clay in polymer matrix makes the polymer amorphous and improves its mechanical strength, thermal stability, gas barriers, fire retardance, corrosion resistance and ionic conductivities.13-24 The exfoliated, intercalated and aggregated phases of MMT in the polymer matrix govern resultant mechanical, thermal, electrochemical and electrical properties.

The investigations of MMT mixed poly(ethylene oxide) (PEO)-alkali metal salt nanocomposite electrolytes synthesized by solution cast technique is currently an intense topic of research for the energy storage/conversion devices.13-17,25-28 It has been established that the exfoliated nanosheets of the MMT in polymer matrix minimize the ions-pairing effect, whereas the intercalated MMT structures impede the polymer crystallization and also enhances the nanometric channels for cations mobility.8,17,25-30

Several attempts were made to reduce the polymer crystallinity by changing the polymer/clay ratio, polymer molecular weight, clay type, amount of metal salt, and/or amount of water introduced in the solid nanocomposites. Stefanescu et al.31,32 demonstrated that the crystallinity of the PEO in such nanocomposites can be tuned by changing the pair of ions contained by the metal salt or the amount of water introduced, when all the other parameters are maintained constant. Yang33 and Aranda et al.34 established that the water contents due to moisture in the PNCEs materials decrease the polymer crystallinity and increases the ionic conduction. As compared to the solution cast technique, the preparation of PNCEs by melt compounded technique is more suitable for their large scale technological applications due to a rapid, least expensive and dry procedure to prepare solvent free polymer electrolyte films.6,14,15,35

Literature survey reveals that so far the PNCEs films of PEO–blend alkaline metal salts-MMT composite have not been synthesized by melt compounded technique. The PEO is an important and exceptional low melting temperature polymer, which acts as a solid solvent in its melt state for many alkaline metal salts. The formation of transient cross-links between the cations and ether oxygen of PEO
repeat units (ion-dipolar interactions) plays the major role to facilitate ion dissociation of the ionic salts. The confirmation of correlation between ionic conductivity and various relaxation processes namely polymer local chain dynamics, ionic conduction relaxation, and electrode polarization relaxation phenomena using broadband dielectric spectroscopy (BDS) is needed to enhance the technological application of the PNCEs materials and promote the science of composites at molecular level. From a practical point of view, dielectric investigations may contribute to the development of methods for handy and reliable assessment of nanocomposites and nanoparticle dispersion as well as silicate layers exfoliation in their on-line process.

In search of novel PNCEs materials, the detailed dielectric/electrical properties and various relaxation processes in the PEO-blend salts (lithium perchlorate trihydrate (LiClO$_4$.3H$_2$O) + sodium perchlorate monohydrate (NaClO$_4$.H$_2$O)-MMT nanoclay films of varying MMT concentration prepared by melt compounded hot-press technique have been studied in the present paper. The blend of alkaline metal salts was used to understand the effect of cations size on the ionic conduction. The polymer chain dynamics in the PNCEs films is an important phenomena in the condensed matter physics of nanoscience to understand the molecular properties of bound water molecules in ion conducting materials on a nanometer scale.

2 Experimental Details

2.1 Materials

The PEO powder of molecular weight 600000 g/mol and polymer grade hydrophilic MMT clay (Nanoclay, PGV, a product of Nanocor$^{18}$), was purchased from Sigma-Aldrich, USA. The MMT is white in colour and has 145 meq/100g cation exchange capacity (CEC), 150–200 aspect ratio (length to width), 2.6 g/cc specific gravity and 9–10 pH value (5% dispersion), which is best recommended clay by the manufacturer for the preparation of PNCEs materials with hydrophilic polymers. Lithium perchlorate trihydrate (LiClO$_4$.3H$_2$O) was purchased from Loba Chemie, India and sodium perchlorate monohydrate (NaClO$_4$.H$_2$O) was purchased from Molychem, India.

2.2 Sample preparation

The PNCEs films were prepared by direct melt compounded technique using 20:1 molar ratio of ethylene oxide (EO) units of PEO to the blend ions (equal number of lithium (Li$^+$) and sodium (Na$^+$) cations) i.e., 80EO:2Li$^+$+2Na$^+$. Firstly, PEO (2.54 g) and blend salt (0.43 g) (LiClO$_4$.3H$_2$O (0.23 g) + NaClO$_4$.H$_2$O (0.20 g)) were taken for the preparation of each sample of 20:1 molar ratio of EO:(Li$^+$+Na$^+$). After that respective amounts of MMT (0.00, 0.025, 0.051, 0.076, 0.127, 0.254 and 0.508 g) for the 0, 1, 2, 3, 5, 10 and 20 wt% MMT concentration with respect to the weight of PEO were taken and mechanically mixed with PEO and blend salts in dry atmosphere for uniform distribution in each sample using an agate mortar and pestle. The melt compounding of the compositions were performed at temperature of 104°C in 60 mm diameter stainless steel die with 1 mm spacer using hot polymer press film making unit under 3 tons pressure and thus melt compounded PNCEs films of thickness ~1 mm were obtained. The melt compounding synthesis of the PNCEs at 104°C is higher than the melting temperatures of PEO and LiClO$_4$.3H$_2$O, that is ~70°C and ~95°C, respectively, but lower than that of NaClO$_4$.H$_2$O (140°C). The resulting free standing flexible-type solid PNCEs films have the general formula (PEO)$_{20}$-(LiClO$_4$.3H$_2$O+NaClO$_4$.H$_2$O–xwt% MMT), where MMT concentration x varies from 0 to 20 wt% with respect to the PEO weight concentration.

2.3 Measurements

Agilent 4284A precision LCR meter, and Agilent 16451B solid dielectric test fixture having a four terminals nickel-plated cobal (an alloy of 17% cobalt + 29% nickel + 54% iron) electrodes of diameter 38 mm, were used for the dielectric measurements in the alternating current field in frequency range 20 Hz-1 MHz. Frequency dependent values of parallel capacitance $C_p$, parallel resistance $R_p$ and loss tangent, tanδ (dissipation factor, D) of the dielectric cell filled with the PNCEs films, were measured for the determination of their frequency dependent dielectric/electrical functions at ambient temperature (~27°C). The exact value of each sample thickness was determined with the micrometer attached with the dielectric test fixture. Prior to the sample measurements, the open circuit calibration of the cell was performed to eliminate the effect of stray capacitance of the cell leads. The details of the evaluation of complex dielectric function $\varepsilon^*(\omega)=\varepsilon'–j\varepsilon''$, complex alternating current (ac) electrical conductivity $\sigma^*(\omega)=\sigma'+j\sigma''$, complex electric modulus $M^*(\omega)=M'+jM''$ and complex impedance $Z^*(\omega)=Z'+jZ''$ of the solid PNCEs films are described by the authors elsewhere.
3 Results and Discussion

3.1 Complex dielectric spectra and MMT structures

Frequency dependent real part of complex dielectric function, ε’ and dielectric loss, ε” spectra of (PEO)\textsubscript{20}−(LiClO\textsubscript{4}.3H\textsubscript{2}O+NaClO\textsubscript{4}.H\textsubscript{2}O)−\textit{x} wt% MMT films decrease non-linearly with the increase of frequency from 20 Hz to 1 MHz (Fig. 1). The large dispersion in the spectra shows the contribution of multiple relaxation processes in these PNCEs materials. These relaxation processes may be corresponding to the PEO molecular polarization, the Maxwell-Wagner interfacial or ionic conduction polarization and the electrode polarization processes in the experimental frequency range, which is mostly observed in the composite materials\textsuperscript{36}.

Dielectric studies of the polymer clay nanocomposites (PCNs) established that the comparative changes in ε’ values with the increase of MMT concentration in the polymer matrix have strong correlation with the MMT intercalated/exfoliated structures\textsuperscript{18−24,37−43}. The dominant phase of intercalated MMT structures in PCNs increases the ε’ value, whereas predominate state of exfoliated MMT structure reduces it\textsuperscript{23,24,37,41-43}. The inset of Fig. 1 shows that the ε’ values at 1 MHz of the studied PNCEs films anomalously vary with the increase of MMT concentration. The small increase in ε’ at 1 and 2 wt% MMT filler is an evidence of predominance state of the intercalated structures, whereas the large decrease in ε’ at 5 wt% and also a significant decrease at 3 and 20 wt% MMT concentration suggests the formation of large amount of exfoliated MMT. The anomalous variation in ε’ may be owing to the formation and uneven distribution of MMT tactoids, and also the change in amount of adsorbed PEO onto these tactoids and the angular oriented state of nano sheets of the exfoliated MMT.

3.2 AC conductivity spectra

Frequency dependent spectra of the real part of ac conductivity σ’ of the melt compounded (PEO)\textsubscript{20}−(LiClO\textsubscript{4}.3H\textsubscript{2}O+NaClO\textsubscript{4}.H\textsubscript{2}O)−\textit{x} wt% MMT films are shown in Fig. 2. These spectra have a dc conductivity plateau in the middle frequency region and exhibit

![Fig. 1 — Frequency dependent real part ε’ and loss ε” of the complex dielectric function of the (PEO)\textsubscript{20}−(LiClO\textsubscript{4}.3H\textsubscript{2}O+NaClO\textsubscript{4}.H\textsubscript{2}O)−\textit{x} wt% MMT nanocomposite electrolytes synthesized by melt compounded technique. Inset shows the variation of ε’ at 1 MHz with wt% MMT concentration](image1)

![Fig. 2 — Frequency dependent real part of ac conductivity σ’ and loss tangent (tanδ) of the (PEO)\textsubscript{20}−(LiClO\textsubscript{4}.3H\textsubscript{2}O+NaClO\textsubscript{4}.H\textsubscript{2}O)−\textit{x} wt% MMT clay nanocomposite electrolytes synthesized by melt compounded technique. The continuous solid line in σ’ spectra represents the fit of experimental data to the Jonscher power law σ(ω)=σ\textsubscript{dc}+Aω\textsuperscript{B}. Inset shows the correlation in ω\textsubscript{p(EP)} value of σ’ and tanδ spectra peak frequency for the 20 wt% MMT film](image2)
conductivity dispersions at lower and higher frequencies. The $\sigma'$ values of the PNCEs films were fitted to the Jonscher power law$^{14}$ $\sigma'(\omega)=\sigma_{dc}+A\omega^n$; where $\sigma_{dc}$ is the dc ionic conductivity, $A$ the pre-exponential factor and $n$ is the fractional exponent ranging between 0 and 1 for the electrolytes. The solid line in the $\sigma'$ spectra (Fig. 2) denotes the fit of experimental data to the power law expression, and the fit values of $\sigma_{dc}$, $A$ and $n$ obtained by Origin® non-linear curve fitting software are presented in Table 1.

It is found that the Jonscher power law is the best fit to the real part of dispersive conductivity at higher frequencies. The deviation from $\sigma_{dc}$ (plateau region) value in lower frequency side of the conductivity spectra is due to the contribution of electrode polarization (EP) process. The EP phenomena occur due to formation of electric double layers (EDLs) (also known as blocking layers) by the free charges that build up at the interface between the dielectric material and the metallic electrode surfaces in plane geometry$^{19,45}$. Recently$^{45,47}$, a physical model of electrode polarization is developed and successfully employed to determine separately the mobile ion concentration and ion mobility of single-ion polymer electrolytes using dielectric relaxation spectroscopy. For electrolytes, $n$ value can be between 1 and 0.5 indicating the ideal long-range pathways and diffusion limited hopping (tortuous pathway) conduction, respectively$^{35}$. The observed $n$ values in the range 0.82-0.87 (Table 1) of the investigated electrolyte films suggest that the long range drift of ions may be one of the processes of ionic conduction.

Table 1 presents that the $\sigma_{dc}$ values of these PNCEs materials decrease nearly by one order of magnitude with the increase of MMT concentration up to 20 wt%. Further for MMT free films, we found that the ionic conductivity of the blend salts added film is lower than that of the unhydrated NaClO$_4$ based film$^{35}$ but higher than that of the unhydrated LiClO$_4$ based film at same salt concentration$^{39}$. This finding suggests that the ionic conductivity of the PNCEs films depend not only on the cation size but also governed by the strength of coordinated cation-polymer interactions. The comparative study of Na$^+$ and Li$^+$ cations transport in a series of PEO based polyurethane ionomers investigated by dielectric relaxation spectroscopy established the lower mobility and conductivity of Li$^+$ ions as compared to that of the Na$^+$, which is due to higher binding energy of the smaller size Li$^+$ with the ether oxygen$^{46}$. Further, in hydrated salts, the presence of three water molecules with Li$^+$ as compared to the one water molecule with Na$^+$ ion, enhances stronger Li$^+$−PEO coordination bridging through water molecules. Hence, the observed ionic-conductivity of the blend salts (Li$^+$+Na$^+$) PNCEs are higher than that of the Li$^+$ ion containing film.

Figure 2 also shows the loss tangent (tanδ) spectra of the PNCEs films of varying MMT concentrations. The tanδ spectra have peaks in the frequency range 10$^{-3}$-10$^7$ Hz, which are corresponding to the electrode polarization relaxation frequency$^{19,22,35,38}$, $f_p$(EP). The $f_p$(EP) values separate the bulk material properties from the large contribution of EP process. Inset of Fig. 2 (for 20 wt% MMT concentration film) shows that the value of $f_p$(EP) corresponds to the tanδ peak, and the frequency at which the low frequency $\sigma'$ spectra deviate from the $\sigma_{dc}$ plateau are the same. This observation confirms the suitability of both the tanδ and $\sigma'$ spectra of these materials for the characterization and analysis of EP phenomena affected frequency region of the PNCEs materials. The electrode polarization relaxation time $\tau_{EP}$, which involves charging and discharging time of the EDLs capacitances is determined by the relation$^{19,22,45,48,50}$ $\tau_{EP}=(2\pi f_p$(EP)$)^{-1}$. The evaluated $\tau_{EP}$ values of the PNCEs films are presented in Table 1.

### 3.3 Electric modulus spectra

The difficulties occurring in the analysis of the complex dielectric function spectra influence from the electrode nature (electrode material), the electrode-specimen electrical contact, and the injection of space charges and the absorbed impurities in the specimen can be resolved by the analysis of electric modulus formalism$^{19,22,24,35,36,51}$. The $M^*$ spectra of the PNCEs
films increase non-linearly with the increase of frequency (Fig. 3), whereas peaks in $M''$ spectra were observed in the upper frequency region. These peaks are attributed to the ionic conduction relaxation frequency, $f_{p(\text{ICR})}$, which correspond to the ionic conduction relaxation process\textsuperscript{19-22,35,51}, and also known as Maxwell-Wagner (MW) interfacial polarization relaxation process. The MW process occurs owing to the free charges build up during the short range electro-migration at the interfacing boundaries of various components of different dielectric constant (or conductivities) in the composite material which results in the formation of nanocapacitors in electrolyte materials\textsuperscript{36}. At sufficient high frequencies, such short range movements of free charges cannot follow the fast changes developed in the applied ac field, and only the molecular polarization is contributed to the dielectric dispersion process. The $f_{p(\text{ICR})}$ separates the change in ions from dc to ac transport. The value of most probable ionic conduction relaxation time, $\tau_0$ is determined by the relation\textsuperscript{51} $\tau_0=\left(2\pi f_{p(\text{ICR})}\right)^{-1}$. The evaluated $\tau_0$ values of the investigated PNCEs films are presented in Table 1.

3.4 Impedance spectra

Figure 4 shows the complex impedance plane plots ($Z''$ versus $Z'$) for the melt compounded PNCEs films. The frequency values of the data points in these plots increase from right to left on the arcs. These plots have a semicircular arc in higher frequency region corresponding to bulk material properties and are followed by a spike in the lower frequency region, which corresponds to the formation of EDLs capacitances at the electrode/sample interface. In the complex impedance plane plots, the extrapolated intercept on the real axis $Z'$ of the common part of two arcs at $f_{p(\text{EP})}$ gives the value of $dc$ resistance, $R_{dc}$ of the electrolyte material\textsuperscript{27,52}. The $R_{dc}$ values of the PNCEs films estimated from the impedance plots are presented in Table 1, which can be used for the evaluation of $\sigma_{dc}$ using the relation $\sigma_{dc}=t/AR_{dc}$, where $t$ is sample thickness and $A$ is the effective electrode surface area. The $R_{dc}$ values of these electrolyte materials increase with the increase of MMT concentration in the range of few kΩ. Table 1 presents the variation in $\sigma_{dc}$ values obtained from power law expression which is according to their $R_{dc}$ values at all the MMT concentrations.

3.5 Correlation between $dc$ ionic conductivity and dielectric relaxation

Generally, the ionic conductivity of an electrolyte, is defined by the relation $\sigma_{dc}=$ $\sum n_i \mu_i q_i$; where $n_i$, $\mu_i$ and $q_i$ refer to the charge carriers density, the ionic mobility, and the charge of $i^{th}$ ion, respectively. In polymer-alkaline metal salt-MMT nanocomposite electrolytes, the polymer chain segmental mobility...
and the barrier produced by the dispersed MMT nano-
platelets for minimizing the ion-pairing effect in the
polymer matrix govern their ionic conductivity at
fixed concentration of the salt. Further, the
enhancement in amorphous phase of polymer also
increases the ionic conductivity of the PNCEs films.
In PEO–MMT nanocomposites, the PEO molecules
entered in MMT galleries impede the PEO
crystallization and also form some kind of tunnel (nanometric channels) that increases the mobility of
cations coordinated with PEO chain.

At ambient temperature, the value $\sigma_{dc}$ of pure
PEG $^{35,55,56}$ is about $10^{-10}$ S cm$^{-1}$, which increases
sharply to 1.54x10$^{-6}$ S cm$^{-1}$ with addition of the blend
of hydrated alkaline metal salts in the molar ratio 20:1
of the EO to the cations (Li$^+$+Na$^+$) (Table 1). The
increase of four order of magnitude of ionic conductivity at very low concentration of the salt
reveals a large dissociation of the blend salts during melt compounding process. It also seems that there is
a decrease in crystalline phase of PEO in the presence
of hydrated salt water molecules, which enhances the
polymer chain segmental mobility and thereby the
ionic conductivity $^{31-35}$. The ionic conductivity of the
studied PNCEs without MMT at ambient temperature
is nearly one order of magnitude higher than that of
the PNCEs prepared with unhydrated salts by solution
cast technique $^{14,27}$. This is mainly owing to the
presence of water molecule of hydrated salts, because the water content increases the ionic conductivity of
the polymer electrolytes $^{31-35}$. At melt compounded
temperature (104°C) of the PNCEs films, there is a
partial dehydration of these salts $^{57}$ and therefore, there
is a large probability of the presence of water
molecules coordinated with cations during the ions
dissociation of the hydrated salts in melt PEO solvent.

Figure 5 shows that the $\sigma_{dc}$ value of (PEO)$_{20}$–
(LiClO$_4$.3H$_2$O+NaClO$_4$.H$_2$O)–x wt% MMT films
decreases by nearly one order of magnitude with the
increase of MMT clay concentration up to 20 wt%. This
is mainly due to the increase in strength of PEO/salts ions/MMT complexations in the presence of the water
molecules. Due to this, the hindrance to the PEO local chain motion increases and hence, there
is decrease of ionic mobility which reduces the ionic
conductivity. Regarding the dynamics of polymer on
one hand, a close contact of polymer segments to a
rigid inorganic structure may slow down their
dynamics where extent and spatial range of this
influences depend on their intermolecular interactions
as well as their chain stiffness. On the other hand,
dimensional restrictions in the nanometer range may
have an effect on the cooperativity of motional process possibly leading to enhanced molecular mobility $^{41,42}$. The increase of $\tau_\sigma$ and $\tau_{EP}$ values (Fig. 5)
of the PNCEs films with the increase of MMT
concentration is expected to increase stiffening of the
PEO segmental motion due to a possible strengthening in the PEO/MMT interactions. It seems
that the water molecules of hydrated salt strengthen
the complexes with the oxyethylene units of PEO
chain and the silanol (Si-O) groups of exfoliated and
intercalated MMT sheets. A good resemblance in
decrease of $\sigma_{dc}$ with the increase of $\tau_{EP}$ and $\tau_\sigma$ values
of the PNCEs materials, confirms that the ionic
conductivity and relaxation processes have strong
correlation, i.e., $\sigma_{dc}$ is almost inversely proportional to
the dielectric relaxation times, which is also found in
earlier study $^{35}$. Recently, Furlani et al. $^{11}$ also confirmed the strong
correlation between the dielectric relaxation times,
relaxation strength and ionic conductivity in lithium
doped polymer electrolytes at ambient temperature.
The small amount of MMT filler in PEO matrix
significantly increases the mechanical and thermal strength of the PEO–MMT nanocomposite materials. Considering this fact along with the $\sigma_{dc}$ values, it can be suggested that the (PEO)$_{20}$–(LiClO$_4$–3H$_2$O+NaClO$_4$–H$_2$O)$\times$ wt% MMT films of very low amount of MMT filler prepared by melt compounded technique at 104°C, may be suitable ion conducting materials of improved mechanical and thermal strength.

### 3.6 AC conductivity scaling properties

Dyre and coworkers attempted various macroscopic and microscopic models of the mobile ions conduction in glasses, polymers, nanocomposites and other disordered solids to explain the physics of dc and ac ions conduction. It has been established that the scaling function of the random barrier model of hopping conduction is universal which means that the shape of master curves of normalized ac conductivity as a function of scaled frequency for all disordered materials at varying composition and temperature obeys time-temperature-concentration superposition.

The scaling behaviour of ac conductivity $\sigma'(\omega)/\sigma_{dc}$, which is also known as normalized ac conductivity can be described by Jonscher power law with the relation $\sigma'(\omega)/\sigma_{dc} = 1 + (\omega/\omega_0)^{n}$; where $\omega_0 = (\sigma_{dc}/A)^{1/n}$ is a characteristic frequency (ionic conduction relaxation frequency) used as scaling parameter for frequency axis. This scaling relation predicts that $\sigma'(\omega)$ starts to rise when the applied frequency is greater than $\omega_0$. Fig. 6 shows the scaling behaviour of $\log(\sigma'_{ac}/\sigma_{dc})$ and $\log(\sigma'/\sigma_{dc})$ versus $\log(\omega/\omega_0)$ of the PNCEs films of different MMT concentration. For these electrolytes, it is found that the scaled ac conductivity spectra almost collapse on a single common curve in the upper frequency region, which represents their ion hopping motion behaviour, whereas deviation in lower frequency range shows the contribution of EP effect. The EP effect corrected scaled behaviour of ac conductivity $\log(\sigma'_{ac}/\sigma_{dc})$ versus $\log(\omega/\omega_0)$, all the curves collapse on a single curve over the entire scaled frequency.

### 3.7 Master curves representation

Figure 7 shows the master curves representation of the real and imaginary parts of the intensive quantities $\varepsilon^*(\omega)$, $M^*(\omega)$ and $\sigma^*(\omega)$ along with tan$\delta$ values of the 1 wt% MMT PNCEs film as one of the representative plots. In this representation, the abrupt upturn in $\varepsilon'$ and $\sigma''$ values is corresponding to the tan$\delta$ peak frequency $f_{EP}$, which shows the contribution of EP effect in the lower frequency spectra up to $f_{EP}$. The intersection of real and imaginary parts of all the intensive quantities occur at $f_{p(MMT)}$, which is corresponding to the ionic conduction relaxation process. The master curve representation (Fig. 7) shows how the various intensive quantities are correlated and can be applied to recognize the various low frequency relaxation processes in complex system.

### 3.8 Transient cross-linked supramolecular structures of the PNCEs materials

On the basis of various experimental results, in general, a number of models have been proposed by considering the Lewis acid-base type polymer/ion/MMT interactions to explain the electrical properties of PNCEs materials. Here we proposed a model by considering the molecular structures of hydrated alkaline salts, and the PEO chain and MMT nanosheets on the basis of experimental dielectric parameters of the investigated PNCEs films to explain this physics.
the effect of various interactions on the polymer chain dynamics and the mechanism of cation conduction.

In hydrated alkaline metal salts, a dynamically disordered water molecules jumping between two distinct positions exists with ion-dipole type interactions in their crystal structures. When dissociation of such salts occurs in melt state of PEO solvent, there is large probability of the existence of water molecules coordinated with cations. The Li$^+$ and Na$^+$ cations have four to six sites of coordination, which results into the complex structures of the composites. In PEO-salt films, the Li$^+$ can coordinate easily with the four neighbour etheric oxygen atoms of the PEO segments as shown in Fig. 8 (Complex-I). In PEO-salt-MMT films, the exfoliated MMT and etheric oxygen of PEO can form the complexes with cation as depicted in Complex-II and Complex-III, but within the MMT phase cations can coordinate with the four oxygen atoms of siloxane (Complex-IV). The presence of water molecules coordinated with the cations of hydrated salt can significantly alter the behaviour of various complexations as shown in Fig. 8 (Complexes-I to -IV).

The MMT concentration dependent real part of dielectric function, the ionic polarization and electrode polarization relaxation times and the ionic conductivity of the studied PNCEs materials and their mutual correlation at microscopic level can be explained by the supramolecular structure with the transient cross-linking between the PEO and exfoliated MMT nanoplatelet via cation and water interactions (complex-V); cations and water coordinated PEO intercalation in MMT gallery (complex-VI). The bridging effect arising due to possible PEO-hydrated cations-exfoliated/intercalated MMT interactions is expected to increase stiffening of the PEO segments.
leading to decrease of polymer segmental chain dynamics and the translation motion of the cations (the migration of cations from one available site to another in the composite matrix, i.e. hopping mechanism). This results in decrease of ionic conductivity. It seems that with increase of MMT concentration, there is also increase of such supramolecular structures, thereby, decreasing the ionic conductivity. Without MMT filler electrolytes, the water molecules of hydrated salt coordinated with cations form the dipole-dipole and ion–dipole type interactions with PEO thereby leading to decrease of PEO crystallinity which is the reason, why the ionic conductivity of PEO-hydrated alkaline metal salt composites are nearly one order of magnitude higher than that of the PEO-unhydrated alkaline metal salt electrolytes. The increase of ionic conductivity due to increase of amorphous phase of PEO with the moisture absorbed water contents was explained by several researchers. In PNCEs of without MMT, it is expected that the anions (ClO$^-_x$) exist somewhere in the polymer backbone as an uncoordinated but due to bulkiness they are rarely contributed in the ionic conduction. But in MMT filled PNCEs, there is large probability of the existence of bulky anions outside the MMT galleries, but however the coordinated cations and water molecules would have natural tendency to enter into nanometric galleries of MMT (intercalated structure) as shown in Complex VI of Fig. 8. As a result, ion pairing is prevented and conduction is through the cations translational motion along the polymer chain. The coordinated water molecules with cations to the PEO chain may help the intercalation process thermodynamically favourable. Further, synthesis of the PNCEs by melt compounded process under pressure, there is a large tendency of the orientation of intercalated/exfoliated MMT nano sheets parallel to the film surface, which decreases the ions conduction paths and hence conductivity decreases with the increase of MMT concentration. The high aspect ratio of MMT platelets is also able to maintain parallelism after intercalation of PEO chain under pressure. The cations mobility will, therefore, depend not only on PEO segmental motion, but also on the potential barrier that the cation must overcome to move from one ion pair to the next. Although, another type of models can be drawn but the model proposed in Fig. 8 is more suitable to explain the ionic conduction and polymer chain dynamics with the increase of MMT concentration in the PEO-blend salts-MMT solid-type electrolytes.

4 Conclusions

This paper reports the detailed dielectric/electrical properties and various relaxation processes in (PEO)$_{20-}(LiClO_4, 3H_2O+NaClO_4, H_2O)–x$ wt% MMT nanocomposite films prepared by melt compounded hot-press technique at 104°C. On the basis of the structural information extracted from the dielectric parameters, the supramolecular structure of the solid-type PNCEs was proposed, and the effect of hydrated salt water molecules on the PEO local chain motion and translation motion of cations was explored. The ionic conductivity of these materials can be tailored within one order of magnitude by adjusting the MMT concentration with improved mechanical and thermal properties. It reveals that the water molecules of hydrated alkaline metal salt play an important role in tuning the electrical properties. The electrical conduction in these nanocomposites was also explained on the basis of transient cross-linked supramolecular structures. The comparative analysis of the various formalisms spectra reveals that the dielectric parameters and the complex structures of the PNCEs materials are strongly coupled properties, which establish the suitability of dielectric relaxation spectroscopy as a novel tool for the online testing and monitoring in the synthesization of PNCEs materials by direct melt compounded technique.

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