

## Temperature dependent dielectric behaviour and structural dynamics of PEO-PMMA blend based plasticized nanocomposite solid polymer electrolyte

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Plasticized nanocomposite solid polymer electrolyte (PNSPE) films comprising polymer blend of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) with lithium triflate ( $\text{LiCF}_3\text{SO}_3$ ) as a dopant ionic salt, propylene carbonate (PC) as plasticizer and montmorillonite (MMT) clay as inorganic nanofiller have been prepared by classical solution-cast and ultrasonic-microwave irradiated solution-cast methods. The X-ray diffraction study confirms predominantly amorphous phase of these PNSPE films having both the intercalated and exfoliated MMT structures. The dielectric and electrical spectra in the frequency range 20 Hz to 1 MHz of the PNSPE films exhibits the relaxation processes corresponding to charging and discharging of electric double layers in the low frequency region and the cations coordinated polymers chain segmental motion in the high frequency region. The complex dielectric permittivity and ac electrical conductivity increase, whereas the impedance values decrease with the increase of temperature of the PNSPE film confirming the thermally activated dielectric and electrical behaviour of the electrolyte material. The temperature dependent dc ionic conductivity and relaxation times of the PNSPE film obey the Arrhenius behaviour of their activation energy values around 0.3 eV. Dielectric parameters reveal that the ions transportation and ionic conductivity in solid ion-dipolar complexes of the PNSPE films are governed by the values of dielectric permittivity and the relaxation times corresponding to structural dynamics. Results of this study infer that the ultrasonic-microwave irradiation processing used during the sample preparation enhances the dielectric permittivity, structural dynamics and ionic conductivity of the PNSPE film as compared to that of the classical solution-cast method prepared film. The ionic conductivity values of these PNSPE films at ambient temperature are found of the order of  $10^{-5} \text{ S cm}^{-1}$  which confirms them as promising electrolyte materials for lithium ion battery and also for all-solid-state ion conducting device applications.

**Keywords:** Polymer blend, Solid polymer electrolyte, Dielectric permittivity, Relaxation time, Ionic conductivity

The solid polymer electrolytes (SPEs) are novel solid-state ion-dipolar complexes having the coordination of a functional group of polymer chain monomer units with the cations of dopant ionic salt<sup>1-26</sup>. The structural amorphicity and dynamics of polymer chain segments play an important role in the ions transportation in the SPE materials. Therefore, characterization of ionic motion coupled with the polymer chain dynamics in the transient-type ion-dipolar complexes of the SPEs consisted of different composition and constituents is currently an intense research field of advanced materials science. In this regard, the dielectric relaxation spectroscopy (DRS) has established as a powerful technique for the characterization of various dielectric polarization processes and their relaxations which govern the ionic conductivity of the SPE materials<sup>1,6-10,12-25</sup>.

The SPEs consisted of poly(ethylene oxide) (PEO) matrix with different lithium salts as ionic dopant

have been frequently investigated owing to the high solvating power of PEO for the alkali metal salts<sup>3-6,8,14-16,18,20-26</sup>. But the high crystalline phase of PEO is its major drawback which is responsible for low ionic conductivity ( $<10^{-5} \text{ S cm}^{-1}$ ) of such SPEs at room temperature (RT). Therefore, several strategies have been adopted in order to increase the amorphous phase of PEO matrix based SPEs for the enhancement of their ionic conductivity at RT up to the required value of conductivity ( $\geq 10^{-5} \text{ S cm}^{-1}$ ) for the device applications. So far, high dielectric permittivity plasticizers and various types of inorganic nanofillers added PEO based SPEs have been extensively investigated as a potential candidate for all-solid-state ion conducting devices<sup>3-5,14,15,18,22,26-28</sup>. Besides the PEO, poly(methyl methacrylate) (PMMA) matrix, which has amorphous phase more than 96%, is also preferred in the preparation of the SPE materials<sup>17,29-34</sup>. But, the brittle property of PMMA matrix based SPE film limits its suitability in designing flexible-type ion-conducting devices of required shapes and sizes.

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Keeping in mind the above mentioned shortcomings of PEO and PMMA matrices, work is in progress on the PEO-PMMA blend matrix based SPE materials because this polymer blend matrix has improved physicochemical properties<sup>1,7,9,20,25,35-39</sup>. The survey of literature reveals that the SPE materials based on PEO-PMMA blend matrix with lithium triflate ( $\text{LiCF}_3\text{SO}_3$ ) as ionic dopant salt, propylene carbonate (PC) as plasticizer and montmorillonite (MMT) clay as inorganic nanofiller have not been studied so far, in order to explore their possible applications as electrolyte material for the ion conducting devices. In search of plasticized nanocomposite solid polymer electrolyte (PNSPE) materials, in this study, an attempt has been made to explore the dielectric polarization and ion-conduction behaviour in (PEO-PMMA)- $\text{LiCF}_3\text{SO}_3$ -PC-MMT films prepared by different methods. The investigations on PEO-MMT and PMMA-MMT nanocomposites<sup>40,41</sup> have already established that the formation of intercalated and exfoliated structures of MMT in the PEO and PMMA matrices improve the thermal, mechanical, gas barrier and corrosion protection properties of these nanocomposite films. Such improvements in the thermo-mechanical properties of SPE materials due to the addition of MMT are also needed for their safe working at elevated temperature, and therefore, the MMT is used as nanofiller in these PNSPEs. The use of lithium triflate salt in preparation of PNSPE materials is also appropriate because it is chemically and thermally stable salt of relatively less sensibility to humidity as compared to other lithium salts. Due to high static dielectric permittivity  $\epsilon_s$  of PC ( $\epsilon_s = 64.52$  at  $25^\circ\text{C}$ )<sup>42</sup>, its use as a plasticizer results in high degree of amorphous phase of the plasticized SPE film due to which more favourable ion conductive paths are formed in the ion-dipolar complexes which are required for fast ion transportations.

In the present paper, the temperature dependent dielectric dispersion and relaxation behaviour of (PEO-PMMA)- $\text{LiCF}_3\text{SO}_3$ -PC-MMT film prepared by the solution-cast method have been investigated both from the academic and technological point of views. The ultrasonication followed by microwave irradiated solution-cast prepared PNSPE film of the same composition has also been studied at RT, in order to confirm the effect of such irradiation processing on the dielectric properties of the SPE material. The ultrasonication processing of the solution plays an

important role in homogeneous dispersion of nanofiller and also in improvement of the degree of miscibility of the polymer blend. The microwave irradiation mainly promotes the salt dissociation and enhances constructive alignment of ion-dipolar complexes during the processing of polymeric electrolyte solution and after that its use in preparation of SPEs by solution-cast method<sup>1,16,17,25</sup>.

## Experimental Procedure

### Sample preparation

The PEO ( $M_w = 6 \times 10^5 \text{ g mol}^{-1}$ ), PMMA ( $M_w = 3.5 \times 10^5 \text{ g mol}^{-1}$ ), hydrophilic MMT clay nanopowder (Nanoclay, PGV, a product of Nanocor®) and  $\text{LiCF}_3\text{SO}_3$  were obtained from Sigma-Aldrich, USA. The propylene carbonate (PC), anhydrous acetonitrile and tetrahydrofuran of spectroscopic grade were purchased from Loba Chemie, India. For the PEO-PMMA blend based PNSPE films, equal weight amounts of PEO and PMMA were used. The [EO + (C=O)]: $\text{Li}^+$ =9:1 stoichiometry was used in preparation of the samples, where EO + (C=O) is the total number of ethylene oxide units (EO) and the carbonyl groups (C=O) of the polymer blend to the lithium cations ( $\text{Li}^+$ ) of the  $\text{LiCF}_3\text{SO}_3$  in the composition. The 10 wt% and 3 wt% amounts of PC and MMT, respectively, to the weight of PEO-PMMA blend were used as a plasticizer and inorganic nanofiller, respectively, in the composition of PNSPE films.

Initially, 1 g amounts of each PEO and PMMA were dissolved in 20 mL amounts of acetonitrile and tetrahydrofuran, respectively, in separate glass bottles. After that, required amounts of  $\text{LiCF}_3\text{SO}_3$ , PC and the MMT were added one by one into the PEO solution, and mixed with continuous magnetic stirring. Finally, in this electrolyte solution, the PMMA solution was mixed and rigorously stirred for 2 h, which resulted in homogeneous (PEO-PMMA)- $\text{LiCF}_3\text{SO}_3$ -10 wt% PC-3 wt% MMT electrolyte solution. After that, this solution was divided into two equal parts. One part of the solution was cast onto Teflon petri dish and by slow evaporation of solvent at room temperature, 'classical' solution cast (SC) method prepared PNSPE film was achieved. For the preparation of ultrasonic-microwave irradiated (US-MW) method electrolyte film, the second part of the electrolyte solution was firstly ultrasonicated (US) using sonicator of 250 W power at 25 kHz frequency for 10 m duration with 15 s ON-OFF step. In this processing, the stainless steel sonotrode was directly immersed into the

electrolyte solution for a strong dose of the ultrasound. After that, the same solution was irradiated by microwave (MW) electromagnetic energy using commercial microwave oven of 600 W power and 2.45 GHz frequency for 2 m duration and 10 s irradiation step with intermediate cooling. Finally, this irradiated electrolyte solution was cast onto Teflon petri dish which resulted in the US–MW method prepared PNSPE film after solvent evaporation.

The surfaces of these SC and US–MW prepared films were found uneven at the micrometer scale, which were made smooth by employing the melt-pressing technique. In this technique, the SC method prepared PNSPE film was placed in circular stainless steel die having 60 mm diameter and 0.26 mm thickness spacer and it was heated up to 80°C in the polymer press (Technosearch Instruments; Model PF–M 15) and then the heater supply was switched-off. Subsequently, the heated material was pressed under 2 tons of pressure per unit area. By slow cooling the melt-pressed material up to room temperature, the PNSPE film of smooth surfaces was achieved. The same steps were used for making the smooth surfaces of US–MW method prepared PNSPE film.

#### Characterizations

The X-ray diffraction (XRD) patterns of the PNSPE films were recorded in reflection mode using a PANalytical X'pert Pro MPD diffractometer of Cu K $\alpha$  radiation (1.5406 Å) operated at 1800 W (45 kV and 40 mA). The scanned step size was kept 0.05° s<sup>-1</sup>.

The dielectric relaxation spectroscopy (DRS) of the PNSPE films was carried out over the frequency range 20 Hz to 1 MHz with 1 V source voltage. Agilent technologies 4284A precision LCR meter along with Agilent 16451B solid dielectric test fixture having active electrode of 38 mm diameter were used for DRS measurements. The dielectric test fixture was placed in a microprocessor-controlled heating chamber for the temperature dependent measurements in the range of 27–55 °C. Frequency dependent values of capacitance  $C_p$ , resistance  $R_p$  and loss tangent ( $\tan\delta = \epsilon''/\epsilon'$ ) of the PNSPE film loaded dielectric fixture were measured in the parallel circuit operation mode and these measured values  $C_p$ ,  $R_p$  and  $\tan\delta$  as a function of frequency  $f$  were used for the determination of dielectric and electrical spectra. Prior the sample measurements, the open circuit calibration of the fixture was performed to eliminate the effect of stray capacitance of the connecting leads. The spectra

of complex dielectric permittivity  $\epsilon^*(\omega) = \epsilon' - j\epsilon''$ , alternating current (ac) electrical conductivity  $\sigma^*(\omega) = \sigma' + j\sigma''$ , electric modulus  $M^*(\omega) = M' + jM''$  and impedance  $Z^*(\omega) = Z' - jZ''$  of the PNSPE films were determined using the expressions described in detail elsewhere<sup>14,17</sup>.

## Results and Discussion

### Structural analysis

The XRD patterns of the SC and US–MW methods prepared PNSPE films over the 2 $\theta$  range from 3.8° to 30° are shown in Fig. 1. The SC method prepared PNSPE film has the broad hump with a tiny peak at 19.03° confirming its predominantly amorphous structure. The XRD pattern of US–MW method prepared PNSPE film have low intensity peaks at 19.18° and 23.19° on the broad background hump which suggests the presence of a little amount of PEO crystalline phase in the highly amorphous structure of the film. Further, diffused peaks appeared around 5° infer some amount of intercalated MMT beside its large exfoliated amount in these PNSPE films. It is concluded because the highly intercalated MMT structures in the polymer matrix exhibit sharp and intense peak towards lower angle side in comparison to the 001 reflection plane peak appeared at 2 $\theta$  = 7.03° of the pristine MMT clay<sup>43</sup>.

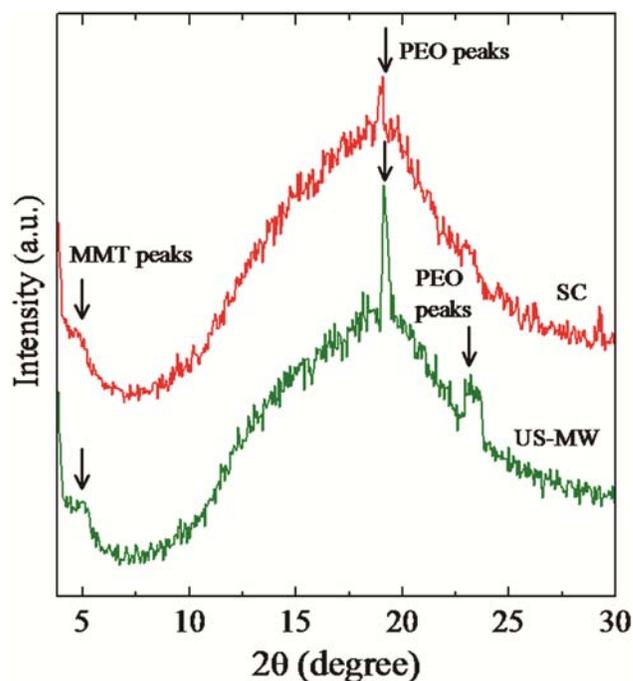


Fig. 1 — The XRD patterns of (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3</sub>-10 wt% PC-3 wt% MMT films prepared by SC and US–MW methods

The pure PEO film exhibits intense and sharp crystalline peaks at  $2\theta = 19.22^\circ$  and  $23.41^\circ$  corresponding to its crystal reflection planes 120 and concerted 112, 032, respectively<sup>43</sup>. The amorphous PMMA film has a broad and diffused peak<sup>17</sup> around  $16^\circ$ , whereas highly crystalline  $\text{LiCF}_3\text{SO}_3$  powder has the characteristic peaks<sup>25</sup> at  $16.62^\circ$ ,  $19.87^\circ$ ,  $20.53^\circ$ ,  $22.77^\circ$  and  $24.71^\circ$ . The absence of  $\text{LiCF}_3\text{SO}_3$  characteristic peaks in the XRD pattern of these PNSPE films (Fig. 1) confirms that there is the total dissolution of the ionic salt in the prepared PNSPE materials. The formation of large range ion-dipolar coordination of the  $\text{Li}^+$  cations with the functional groups of PEO and PMMA and also with the dipolar group of PC results in complete dissociation of the ionic salt and these interactions turned the SC method prepared material into the amorphous phase. But, the presence of both the PEO peaks of very low intensity in case of US-MW method prepared electrolyte film suggests that the ultrasonication followed by microwave irradiation processing liberates a few number of the ether oxygen units of PEO chains from the ion-dipolar complexes. Such liberated ether oxygen units form some crystalline domains of PEO in the PNSPE material, although these domains are insignificant in comparison to the total amount of amorphous phase of the material.

#### Dielectric and electrical dispersion

The temperature dependent complex dielectric permittivity (real part  $\epsilon'$  and dielectric loss  $\epsilon''$ ), ac electrical conductivity (real part  $\sigma'$  and loss part  $\sigma''$ ) and the dielectric loss tangent ( $\tan\delta = \epsilon''/\epsilon'$ ) spectra of (PEO-PMMA)- $\text{LiCF}_3\text{SO}_3$ -10 wt% PC-3 wt% MMT film prepared by SC method are shown in Fig. 2. These spectra have some interesting characteristics features related to the dielectric polarization processes and their relaxations in the solid ion-dipolar complexes. Firstly, there is a large increase of  $\epsilon'$  and  $\epsilon''$  values with the decrease of frequency which is owing to the dominance of electrode polarization (EP) effect over the bulk properties. This EP effect is an unwanted phenomenon commonly occurring in the SPE materials during their dielectric measurements. Under the influence of the slowly varying electric field, accumulation of ions at the electrode/electrolyte interface occurs, which results in the formation of electric double layers (EDLs) near the dielectric test fixture electrode surfaces<sup>1,6,8,10,12-16,21-23</sup>. Secondly, the  $\epsilon'$  spectra of the film have a point of inflection around

1 kHz and the high frequency dispersion approaches steady state near 1 MHz. This frequency region represents the dipolar polarization process in the ion-dipolar complexes. Therefore, it is reasonable to consider the  $\epsilon'$  values of the electrolyte at 1 kHz and 1 MHz frequencies equal to their static dielectric permittivity  $\epsilon_s$  and the limiting high frequency

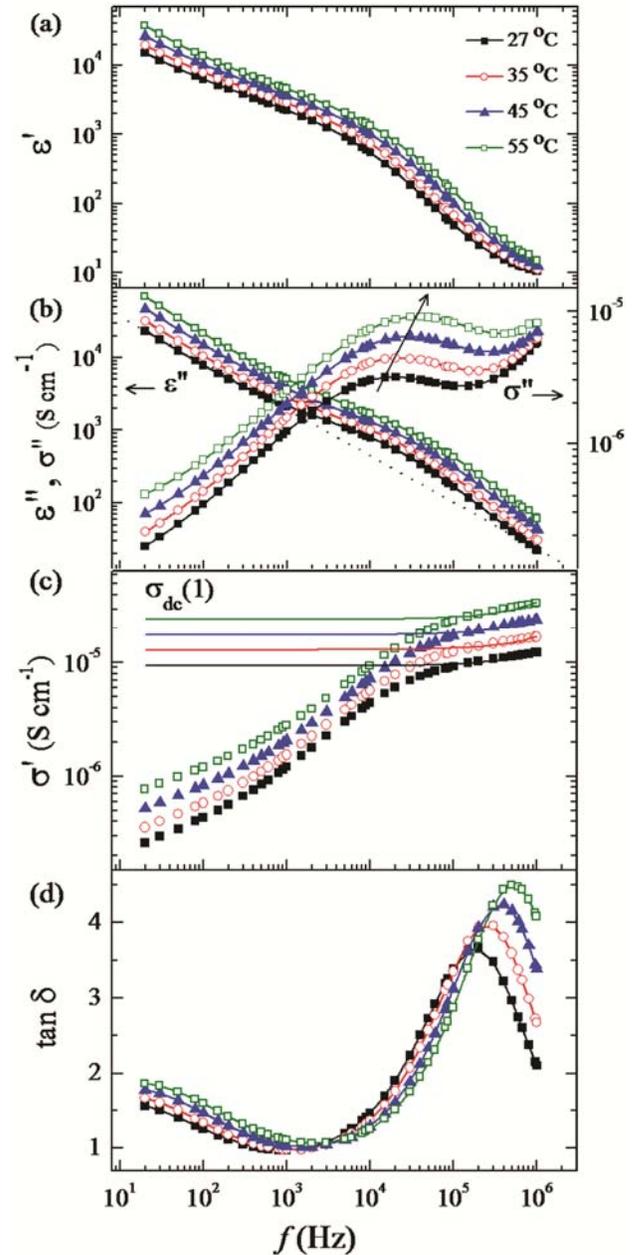


Fig. 2 — Frequency dependent spectra of (a)  $\epsilon'$ , (b)  $\epsilon''$  and  $\sigma''$ , (c)  $\sigma'$  and; (d) dielectric loss tangent ( $\tan\delta = \epsilon''/\epsilon'$ ) of SC method prepared (PEO-PMMA)- $\text{LiCF}_3\text{SO}_3$ -10 wt% PC-3 wt% MMT film at different temperatures. The solid lines in  $\sigma'$  spectra represent the Jonscher's power law fit to the experimental data at high frequencies

permittivity  $\epsilon_\infty$ , respectively. The observed values of  $\epsilon_s$ ,  $\epsilon_\infty$  and the dielectric relaxation strength  $\Delta\epsilon = \epsilon_s - \epsilon_\infty$  of the SC method prepared PNSPE film at different temperatures are recorded in Table 1.

Figure 2(a,b) shows that the  $\epsilon'$  and  $\epsilon''$  spectra gradually increase with increasing temperature of the PNSPE film, which is attributed to the increase in all the dielectric polarization processes of the material. The increase of temperature enhances the free volume and degree of polymer chain flexibility which favours the dipolar orientation and the constructive alignment of ion-dipolar bonding resulting in the increase of dielectric polarization. Further, the  $\epsilon''$  spectra on log-log scale show deviation from linearity (dotted line) which starts from 1 kHz and extend up to 500 kHz. The enhanced  $\epsilon''$  values from linearity confirm the contribution of relaxation processes associated with the EDLs and also the polymer chain segmental dynamics, but the relaxation peaks corresponding to these dynamics have not appeared in the  $\epsilon''$  spectra. To explore the temperature dependent behaviour of EDL dynamics, the imaginary part  $\sigma''$  of ac conductivity spectra has also been plotted along with the  $\epsilon''$  spectra in Fig. 2(b). The temperature dependent  $\sigma''$  spectra of the PNSPE film exhibit relaxation peaks in the frequency range 10 kHz - 100 kHz, which can be assigned to the charging and discharging dynamical process of EDLs<sup>10</sup>. Further, the  $\sigma''$  peak has shifted towards higher frequency side with the increase of temperature as indicated by an arrow in the figure, which confirms that the EDL dynamics is a thermally activated process for the PNSPE film. The value of relaxation time  $\tau_{EP}$  or  $\tau_{EDL}$  corresponding to EDL dynamics in the electrolyte material is determined from the relation  $\tau_{EDL} = 1/(2\pi$

$f_{p(\sigma'')})$ , where  $f_{p(\sigma'')}$  is the value of frequency at  $\sigma''$  peak. The temperature dependent  $\tau_{EP}$  values of SC method prepared PNSPE film are found of the order of  $\mu$ s duration, which have a decrease with the increasing temperature of the film (Table 1).

Figure 2(c) depicts the  $\sigma'$  (real part of ac conductivity) spectra of SC method prepared PNSPE film at different temperatures. The  $\sigma'$  values of the PNSPE film increase non-linearly with the increase of the frequency of the ac electric field of measurements. It is observed that the high frequencies  $\sigma'$  values of the PNSPE film obey the Jonscher's power law<sup>44</sup>  $\sigma'(\omega) = \sigma_{dc} + A\omega^n$ , where  $\sigma_{dc}$  is the dc ionic conductivity,  $A$  is the pre-exponential factor and  $n$  is the fractional exponent ranging between 0 and 1. The power law fit  $\sigma'$  values at different temperatures are shown by solid lines (Fig. 2(c)). It is found that the experimental  $\sigma'$  values start to deviate from fit lines below 100 kHz and the value of deviation increases with the further decrease in frequency by more than one order of magnitude. This confirms that the EDL acts as blocking electrode and greatly reduces the ionic conductivity of the ion-conducting PNSPE material at low frequencies. The temperature dependent values of  $\sigma_{dc}$  (denoted as  $\sigma_{dc}(1)$ ) and  $n$  of the PNSPE film obtained from power law fit are given in Table 1. Further, the  $\sigma'$  values of the PNSPE film have uniform increase over the entire frequency range with increasing temperature of the film. This increase in the  $\sigma'$  values is owing to the enhancement of ions mobility with the increase of temperature. As revealed from the XRD spectra that the total amount of added salt has already been dissociated in the composite material, and hence, the increase of temperature does not

Table 1 — Values of static dielectric permittivity  $\epsilon_s$  (i.e.,  $\epsilon'$  at 1 kHz), high frequency limiting permittivity  $\epsilon_\infty$  (i.e.,  $\epsilon'$  at 1 MHz), dielectric relaxation strength  $\Delta\epsilon$ , EDL relaxation time  $\tau_{EP}$ , loss tangent relaxation time  $\tau_{\tan\delta}$ , dc ionic conductivity  $\sigma_{dc}(1)$  and  $\sigma_{dc}(2)$  determined from power law fit and impedance spectra, respectively, and fractional exponent  $n$  at various temperatures of (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3</sub>-10 wt% PC-3 wt% MMT film prepared by SC method and at 27°C for the film prepared by US-MW method

Temperature (°C)	$\epsilon_s$	$\epsilon_\infty$	$\Delta\epsilon$	$\tau_{EP}$ ( $\mu$ s)	$\tau_{\tan\delta}$ ( $\mu$ s)	$\sigma_{dc}(1) \times 10^5$ (S cm <sup>-1</sup> )	$\sigma_{dc}(2) \times 10^5$ (S cm <sup>-1</sup> )	$n$
SC method prepared PNSPE film								
27	2225.9	10.5	2215.4	10.62	0.88	0.93	1.12	0.88
35	2823.5	11.4	2812.1	7.94	0.62	1.29	1.55	0.90
45	3597.1	12.8	3584.3	5.91	0.42	1.75	2.18	0.94
55	4537.7	14.8	4522.9	4.47	0.30	2.44	2.98	0.96
US-MW method prepared PNSPE film								
27	3296.6	10.1	3286.5	7.92	0.54	1.50	1.70	0.89

contribute to the mobile ions concentration. Therefore, it seems that the increase of temperature results in enhancement of vacant sites favourable for the ions transportation with enhanced mobility, which in turn increases the ionic conductivity of the PNSPE film which is a common characteristic of the SPE materials<sup>3,19,22</sup>. Table 1 shows that the temperature dependent  $n$  values of the PNSPE film are in the range 0.88 to 0.96 which are less than unity suggesting that the ions transportation in solid ion-dipolar complexes has mainly occurred through hopping mechanism<sup>6,19,45</sup>. Further,  $n$  values of the PNSPE film have an increase with the increase of temperature, which confirms that the strength of ion-ion and ion-dipolar interactions decreases as the temperature of the PNSPE film increases.

The  $\tan\delta$  ( $= \epsilon''/\epsilon'$ ) spectra of SC method prepared PNSPE film at different temperatures exhibit the Debye-type relaxation peak in the high frequency region (Fig. 2d). These peaks represent the polymer chain segmental relaxation process in the transient ion-dipolar complexes of the electrolyte. The single and sharp peak of  $\tan\delta$  spectra also reveals that there is the cooperative motion of the PEO and PMMA chains segments because of their coupling through ion-dipolar coordination. The magnitude of these relaxation peaks has a gradual increase and their position shift towards higher frequency side with the increase of temperature of the film. This temperature dependent behaviour of  $\tan\delta$  peak confirms that the polymer chain segmental dynamics increases due to the enhancement of structural flexibility in the complexes as the temperature of PNSPE film increases. Using the values of  $\tan\delta$  peak frequencies  $f_{p(\tan\delta)}$ , the values of relaxation time  $\tau_{\tan\delta}$  corresponding to the polymer chain segmental dynamics (as also denoted by  $\tau_s$ )<sup>23</sup> are determined by the relation  $\tau_{\tan\delta} = 1/2\pi f_{p(\tan\delta)}$ . The temperature dependent  $\tau_{\tan\delta}$  values of the PNSPE film prepared by SC method are given in Table 1. As compared to the  $\tau_{EP}$  values of the film, its  $\tau_{\tan\delta}$  values are found low which reveals that the EDL dynamics is relatively slower than the polymer chain segmental dynamics but their variation is identical which confirm that these processes have some mutual correlation.

Figure 3 shows the electric modulus (real part  $M'$  and loss  $M''$ ) spectra of SC method prepared PNSPE film at different temperatures. The  $M'$  and  $M''$  spectra of the studied PNSPE film exhibit dispersion above

100 kHz which is in the frequency region of polymer chain segmental relaxation process, whereas in the EP effect dominated frequency region, i.e., below 10 kHz, their values are zero because the  $M^*(\omega)$  and  $\epsilon^*(\omega)$  product has unity value. Mostly, the  $M''$  spectra of the ion conducting SPE materials exhibit a relaxation peak in the high frequency region corresponding to the ionic conductivity relaxation process<sup>6,7,12,14,21,23,25</sup>. But, for the studied PNSPE film, it seems that the  $M''$  spectra might exhibit a conductivity relaxation peak above the present experimental frequency range, i.e., 1 MHz. Further, with an increase of temperature of the PNSPE film, its  $M'$  and  $M''$  dispersion also shift towards higher frequency side which is in agreement with the temperature dependent dispersion behaviour of electric modulus spectra of various SPEs<sup>6,7,12,14</sup>.

The Nyquist impedance plots ( $Z''$  versus  $Z'$ ) of the SC method prepared (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3</sub>-10 wt% PC-3 wt% MMT film at different temperatures are depicted in Fig. 4. These impedance plots are commonly used for the electrochemical characterization of the ion conducting materials<sup>17,19,21,46</sup>.

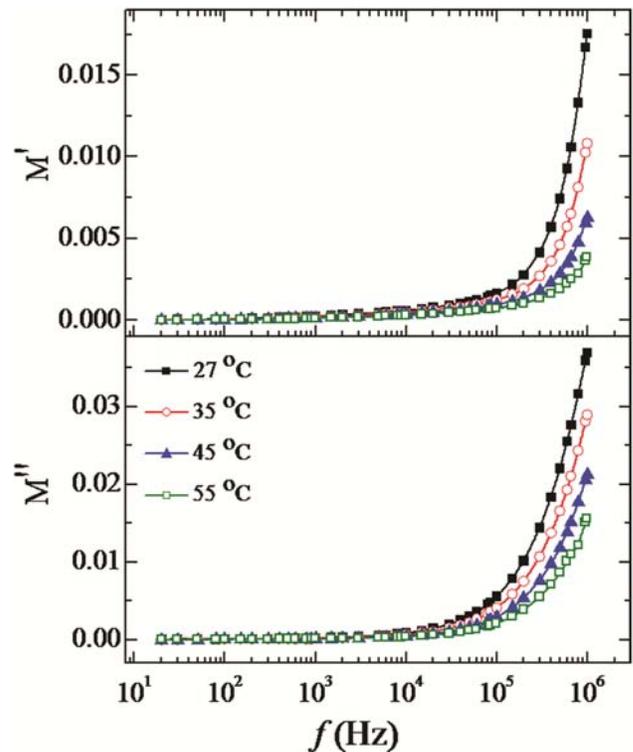


Fig. 3 — Frequency dependent spectra of real part  $M'$  and loss  $M''$  of complex electric modulus of SC method prepared (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3</sub>-10 wt% PC-3 wt% MMT film at different temperatures

The impedance plots of the SPE materials commonly exhibit a spike in the low frequency region due to the capacitive behaviour of EDLs and an arc in the high frequency region corresponding to bulk properties which can also be seen in the inset of Fig. 4 of the studied PNSPE film. The size of the arc reduces and also have shifted towards lower resistance on the real axis with increasing temperature of the film which is temperature dependent characteristic behaviour of the SPE materials<sup>17,19</sup>. Further, such materials can be represented by an equivalent electrical circuit having parallel combination of bulk resistance  $R_b$  and geometrical capacitance  $C_g$  with a constant phase element CPE in series<sup>19</sup>. The  $R_b$  values of the PNSPE film at various temperatures are indicated by vertical lines on real axis of the impedance plots as shown in the inset of the figure. The  $\sigma_{dc}$  value of the PNSPE film can also be determined using the relation  $\sigma_{dc} = t_s/R_b A$ , where  $t_s$  is the thickness and  $A$  is the surface area of the film that is equal to the surface area of active electrode of the dielectric test fixture. The  $\sigma_{dc}$  values determined from  $R_b$  values of the PNSPE film at different temperatures are denoted by  $\sigma_{dc}(2)$  and the same are recorded in Table 1. These  $\sigma_{dc}(2)$  values are found slightly higher than those of the corresponding  $\sigma_{dc}(1)$  values of the same electrolyte film, which reveals that the  $\sigma_{dc}$  values of a SPE film may differ slightly with the choice of its determination method.

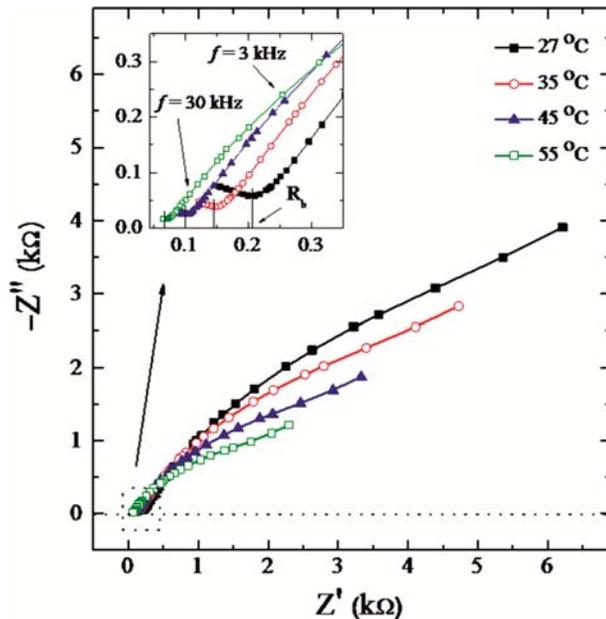


Fig. 4 — Complex impedance plane plots ( $Z''$  vs  $Z'$ ) of SC method prepared (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3</sub>-10 wt% PC-3 wt% MMT film at different temperatures. Inset shows the enlarged view of plots at high frequencies

#### Correlation of ionic conductivity with dielectric parameters

Figure 5 shows the temperature dependent  $\Delta\epsilon$ ,  $\tau_{EP}$  ( $\tau_{EDL}$ ),  $\tau_{tan\delta}$  ( $\tau_s$ ) and  $\sigma_{dc}$  values of the (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3</sub>-10 wt% PC-3 wt% MMT film prepared by SC method. On a logarithmic scale, the values of these dielectric and electrical parameters have a linear variation with the reciprocal of temperature which confirms their Arrhenius-type behaviour. The decrease of both the relaxation times ( $\tau_{EP}$  and  $\tau_s$ ) and the increase of  $\Delta\epsilon$  values with increasing temperature favours the enhancement of ionic conductivity of the PNSPE film with the increase of its temperature. The increase of temperature introduces more flexibility in the cations coordinated polymer chain segments as the free volume increases, and thereby increase the cations mobility which favours in the increase of ionic conductivity of such kind of SPE materials<sup>6,16,23-25</sup>. These results clearly indicate that besides the polymer chain segmental dynamics in ion-dipolar complexes, the EDL dynamics also have similar kind of correlation with the ionic conductivity of the investigated PNSPE film.

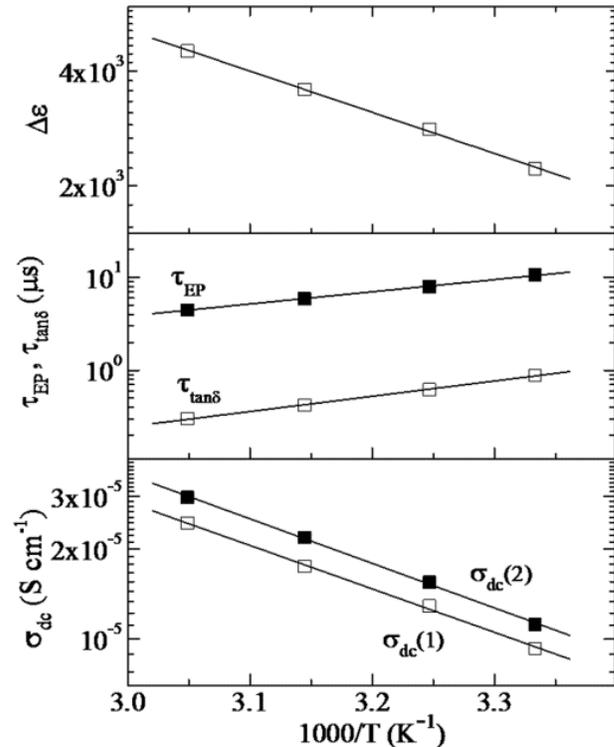


Fig. 5 — Reciprocal temperature dependence of dielectric relaxation strength  $\Delta\epsilon$ , electrode polarization relaxation time  $\tau_{EP}$ , loss tangent relaxation time  $\tau_{tan\delta}$ , and dc ionic conductivity  $\sigma_{dc}$  ( $\sigma_{dc}(1)$  and  $\sigma_{dc}(2)$  determined from power law fit and impedance spectra, respectively) of SC method prepared (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3</sub>-10 wt% PC-3 wt% MMT film

The values of conductivity activation energy  $E_\sigma$  and dielectric relaxation activation energy  $E_\tau$  of the PNSPE film prepared by SC method are determined by the relations  $\sigma_{dc} = \sigma_0 \exp(-E_\sigma/k_B T)$  and  $\tau = \tau_0 \exp(E_\tau/k_B T)$ , respectively, where  $\sigma_0$  and  $\tau_0$  are pre-exponent factors,  $k_B$  is the Boltzmann's constant and  $T$  is the temperature in absolute scale. The  $E_\sigma$  and  $E_\tau$  values of the PNSPE film are found 0.29 and 0.33 eV, respectively. These activation energy values are in consistent with several other SPE materials<sup>2,18,22,25</sup>. The low values of activation energies suggest that the ions hopping mechanism occurs relatively fast in the investigated ion-dipolar complexes of the PNSPE film which is due to the transient coupling between the mobile cations and the dynamical polymer chain segments. Further, the  $E_\sigma$  and  $E_\tau$  values of the SC method prepared PNSPE film are nearly equal confirming that the ions have to overcome the same energy barrier while relaxing as well as while conducting, i.e., the chain segmental motion and the ions hopping mechanisms contribute equally in the ionic conductivity of the PNSPE material.

The literature survey shows that the PEO-LiCF<sub>3</sub>SO<sub>3</sub> films have  $\sigma_{dc}$  values<sup>6,10,47-51</sup> in the range of  $\sim 10^{-7}$ - $10^{-9}$  S cm<sup>-1</sup> at RT. Two orders of magnitude variation in the  $\sigma_{dc}$  values of these films are due to the concentration variation of the salt, the differences in sample preparation methods and different procedures used for the determination of ionic conductivity. The  $\sigma_{dc}$  values of these films further increase by one to two orders of magnitude with the addition of plasticizers, namely ethylene carbonate (EC) and propylene carbonate (PC), and also inorganic nanofillers like alumina (Al<sub>2</sub>O<sub>3</sub>), silica (SiO<sub>2</sub>) and organomodified montmorillonite (OMMT) clay<sup>46-48,52</sup>. The  $\sigma_{dc}$  values of the PMMA-LiCF<sub>3</sub>SO<sub>3</sub> film at RT are of the order of  $\sim 10^{-6}$  S cm<sup>-1</sup>, which are also increased by one to two orders of magnitude by the addition of appropriate amount of EC and PC plasticizers<sup>33,34,53</sup>. The investigated (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3</sub>-10 wt% PC-3 wt% MMT film has  $\sigma_{dc}$  value  $\sim 10^{-5}$  S cm<sup>-1</sup> at RT (Table 1), which reveals that the PEO-PMMA blend matrix is a novel material for the preparation of solid polymer electrolytes of required ionic conductivity for practical device applications.

#### Effect of sample preparation methods

Figure 6 shows the  $\epsilon'$ ,  $\epsilon''$ ,  $\sigma'$ ,  $\sigma''$  and  $\tan\delta$  spectra of the (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3</sub>-10 wt% PC-3 wt% MMT films prepared through SC and US-MW methods. A noticeable increase is found in these

spectra when the PNSPE film is prepared by US-MW method as compared to that of the same composition prepared by SC method. The values of various dielectric parameters ( $\epsilon_s$ ,  $\epsilon_\infty$ ,  $\Delta\epsilon$ ,  $\tau_{EP}$ ,  $\tau_{\tan\delta}$  and  $\sigma_{dc}$ ) of the US-MW method prepared PNSPE film at RT (27°C) are determined and these values are given in Table 1. From Table 1, it is found that the  $\epsilon_s$  and  $\sigma_{dc}$  values of US-MW method prepared PNSPE film have

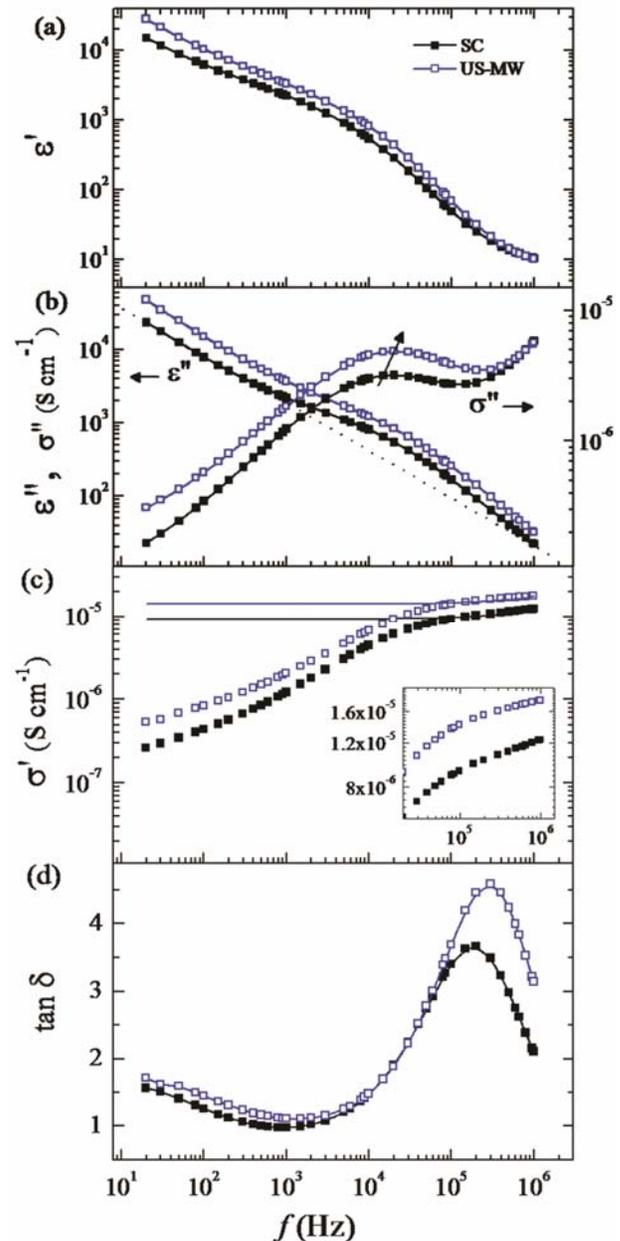


Fig. 6 — Frequency dependent spectra of (a)  $\epsilon'$ , (b)  $\epsilon''$  and  $\sigma''$ , (c)  $\sigma'$  and; (d) dielectric loss tangent ( $\tan\delta = \epsilon''/\epsilon'$ ) of SC and US-MW methods prepared (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3</sub>-10 wt% PC-3 wt% MMT films at RT. Inset shows the enlarged view of  $\sigma'$  plot at high frequencies

increased by about 1.5 times as compared to those of the SC method prepared PNSPE film of the same composition. Further, the  $\tau_{EP}$  and  $\tau_{\tan\delta}$  values of the US–MW method prepared PNSPE film have decreased by about 25% and 40%, respectively, as compared to that of the SC method prepared PNSPE film. These results confirm that the increase of  $\sigma_{dc}$  value of the US–MW method prepared PNSPE film is due to its relatively low value of relaxation times and the high value of dielectric permittivity. The relatively 1.5 times increase in  $\epsilon_s$  value of US–MW method prepared PNSPE film reveals that the US–MW processing of the solution enhances the number of parallel dipolar ordering per unit volume, i.e., align the dipoles in constructive mode. It is expected because the dipolar reorientation in polymeric solutions occurs at microwave frequencies<sup>54</sup>. Further, it seems that in such constructively aligned ion-dipolar structures, the cooperative dipolar segmental dynamics of the polymer increase as revealed from the decrease of  $\tau$  values which promotes the ions transportation by hopping mechanism and due to this fact there is enhancement of  $\sigma_{dc}$  value of the US–MW method prepared PNSPE film as compared to that of the SC method prepared PNSPE film.

Figure 7 shows the  $Z''$  vs  $Z'$  plots of the PNSPE films having the same composition but prepared by

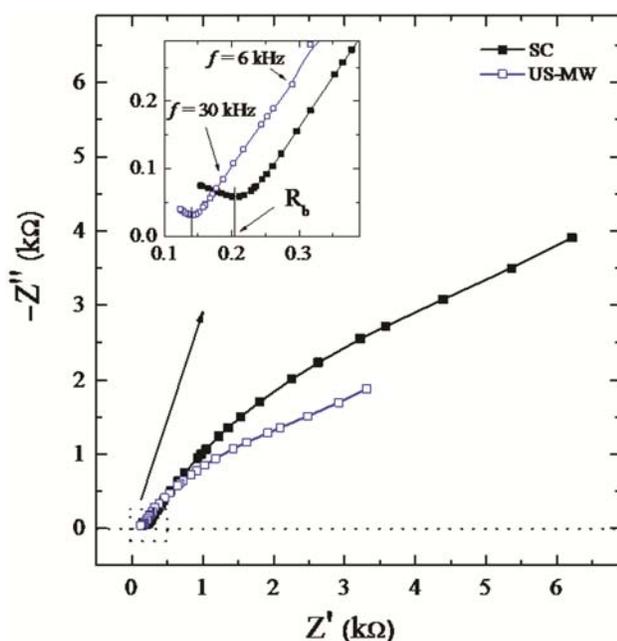


Fig. 7 — Complex impedance plane plots ( $Z''$  vs  $Z'$ ) of SC and US–MW methods prepared (PEO–PMMA)–LiCF<sub>3</sub>SO<sub>3</sub>–10 wt% PC–3 wt% MMT films at RT. Inset shows the enlarged view of plots at high frequencies

SC and US–MW methods. Inset of figure infers that the  $Z'$  values of the US–MW method prepared film are relatively low in the high frequency region. Therefore, the  $\sigma_{dc}(2)$  value of the US–MW method prepared PNSPE film is found relatively high as compared to the SC method prepared PNSPE film (Table 1). As discussed above from the XRD patterns of these PNSPE films (Fig. 1), that the US–MW method prepared PNSPE film has few PEO crystallites. But its high  $\sigma_{dc}$  value as compared to the SC method prepared PNSPE film suggests that the US–MW processing of the material produces more favourable ion conductive paths which mask the effect of PEO crystallites in regards to the enhancement of the ionic conductivity in such PNSPE material when the sample is prepared by US–MW method.

## Conclusions

The temperature dependent dielectric and electrical properties of predominantly amorphous type (PEO–PMMA)–LiCF<sub>3</sub>SO<sub>3</sub>–10 wt% PC–3 wt% MMT film prepared by SC method were reported. The ionic conductivity values of the investigated PNSPE film at various temperatures is governed by the values of its dielectric permittivity and the relaxation time of the polymer chain segmental motion. Dielectric properties confirm that the transportation of lithium ions occurs through hopping mechanism in these solid ion-dipolar complexes. The conductivity and relaxation activation energies of the PNSPE are found nearly same, i.e., 0.3 eV which confirms the equal energy barrier for ions while conducting as well as relaxing in the ion-dipolar complexes. The dielectric and electrical properties of the same composition PNSPE film were significantly increased when it was prepared using US–MW irradiated electrolyte solution. The observed ionic conductivity value of the order of  $10^{-5}$  S cm<sup>-1</sup> of these different methods prepared PEO–PMMA blend based PNSPE films at RT confirms their suitability as an electrolyte material for the solid-state lithium ion batteries.

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## References

- 1 Sengwa R J, Dhatarwal P & Choudhary S, *Electrochim Acta*, 142 (2014) 359-370.
- 2 Chandra A, Chandra A & Thakur K, *Eur Phys J Appl Phys*, 69 (2015) 20901(1-6).
- 3 Choudhary S & Sengwa R J, *Indian J Eng Mater Sci*, 21 (2014) 7-15.
- 4 Kumar Y, Hashmi S A & Pandey G P, *Solid State Ionics*, 201 (2011) 73-80.
- 5 Ngai K S, Ramesh S, Ramesh K & Juan J C, *Ionics*, 22 (2016) 1259-1279.
- 6 Karmakar A & Ghosh A, *J Appl Phys*, 107 (2010) 104113(1-6).
- 7 Sharma P & Kanchan D K, *Polym Int*, 63 (2014) 290-295.
- 8 Karmakar A & Ghosh A, *Curr Appl Phys*, 12 (2012) 539-543.
- 9 Sharma P & Kanchan D K, *Ionics*, 19 (2013) 1285-1290.
- 10 Karan N K, Pradhan D K, Thomas R, Natesan B & Katiyar R S, *Solid State Ionics*, 179 (2008) 689-696.
- 11 Deka M & Kumar A, *J Solid State Electrochem*, 17 (2013) 977-986.
- 12 Pradhan D K, Choudhary R N P & Samantaray B K, *Mater Chem Phys*, 115 (2009) 557-561.
- 13 Ramesh S, Liew C W & Ramesh K, *J Appl Polym Sci*, 127 (2013) 2380-2388.
- 14 Sengwa R J, Sankhla S & Choudhary S, *Ionics*, 16 (2010) 697-707.
- 15 Choudhary S & Sengwa R J, *Ionics*, 17 (2011) 811-819.
- 16 Choudhary S & Sengwa R J, *Mater Chem Phys*, 142 (2013) 172-181.
- 17 Sengwa R J & Choudhary S, *J Phys Chem Solids*, 75 (2014) 765-774.
- 18 Sengwa R J & Choudhary S, *Indian J Phys*, 88 (2014) 461-470.
- 19 Nath A K & Kumar A, *Electrochim Acta*, 129 (2014) 177-186.
- 20 Choudhary S & Sengwa R J, *J Appl Polym Sci*, 132 (2015) 41311.
- 21 Chilaka N & Ghosh S, *Electrochim Acta*, 134 (2014) 232-241.
- 22 Kumar M & Srivastava N, *J Non-Cryst Solids*, 389 (2014) 28-34.
- 23 Zhang S, Dou S, Colby R H & Runt J, *J Non-Cryst Solids*, 351 (2005) 2825-2830.
- 24 Munar A, Andrio A, Iserte R & Compañ V, *J Non-Cryst Solids*, 357 (2011) 3064-3069.
- 25 Sengwa R J, Choudhary S & Dhatarwal P, *Ionics*, 21 (2015) 95-109.
- 26 Mejía A, García N, Guzmán J & Tiemblo P, *Solid State Ionics*, 261 (2014) 74-80.
- 27 Köster T K J & Wullen L V, *Solid State Ionics*, 181 (2010) 489-495.
- 28 Johan M R & Fen L B, *Ionics*, 16 (2010) 335-338.
- 29 Meneghetti P, Qutubuddin S & Webber A, *Electrochim Acta*, 49 (2004) 4923-4931.
- 30 Shukla N & Thakur A K, *Solid State Ionics*, 181 (2010) 921-932.
- 31 Deka M & Kumar A, *Electrochim Acta*, 55 (2010) 1836-1842.
- 32 Ramesh S & Wong K C, *Ionics*, 15 (2009) 249-254.
- 33 Ali A M M, Yahya M Z A, Bahron H, Subban R H Y, Harun M K & Atan I, *Mater Lett*, 61 (2007) 2026-2029.
- 34 Ramesh S & Wen L C, *Ionics*, 16 (2010) 255-262.
- 35 Rajendran S, Kannan R & Mahendran O, *J Power Sources*, 96 (2001) 406-410.
- 36 Shanmukaraj D, Wang G X, Murugan R & Liu H K, *J Phys Chem Solids*, 69 (2008) 243-248.
- 37 Tan S M & Johan M R, *Ionics*, 17 (2011) 485-490.
- 38 Jeddi K, Qazvini N T, Jafari S H & Khonakdar H A, *J Polym Sci Part B: Polym Phys*, 48 (2010) 2065-2071.
- 39 Ghelichi M, Qazvini N T, Jafari S H, Khonakdar H A, Farajollahi Y & Scheffler C, *J Appl Polym Sci*, 129 (2013) 1868-1874.
- 40 Miwa Y, Drews A R & Schlick S, *Macromolecules*, 41 (2008) 4701-4708.
- 41 Zhu J, Start P, Mauritz K A & Wilkie C A, *Polym Degrad Stabil*, 77 (2002) 253-258.
- 42 Sengwa R J, Choudhary S & Dhatarwal P, *J Mol Liq*, 225 (2017) 42-49.
- 43 Choudhary S & Sengwa R J, *J Appl Polym Sci*, 131 (2014) 39898.
- 44 Jonscher A K, *Dielectric relaxation in solids* (Chelsea Dielectric Press, London), 1983.
- 45 Dyre J C & Schrøder T B, *Rev Mod Phys*, 72 (2000) 873-892.
- 46 Qian X, Gu N, Cheng Z, Yang X, Wang E & Dong S, *J Solid State Electrochem*, 6 (2001) 8-15.
- 47 H W Chen & F C Chang, *Polymer* 42 (2001) 9763-9769.
- 48 Choudhary S & Sengwa R J, *Indian J Pure Appl Phys*, 49 (2011) 600-605.
- 49 Pitawala H M J C, Dissanayake M A K L, Seneviratne V A, Mellander B E & Albinson I, *J Solid State Electrochem*, 12 (2008) 783-789.
- 50 Frech R & Chintapalli S, *Solid State Ionics*, 85 (1996) 61-66.
- 51 Appetecchi G B, Croce F, Hassoun J, Scrosati B, Saloman M & Cassel F, *J Power Sources*, 114 (2003) 105-112.
- 52 Johan M R, Shy O H, Ibrahim S, Yassin S M M & Hui T Y, *Solid State Ionics*, 196 (2011) 41-47.
- 53 Ahmad S, Saxena T K, Ahmad S & Agnihotry S A, *J Power Sources*, 159 (2006) 205-209.
- 54 Shinyashiki N, Sengwa R J, Tsubotani S, Nakamura H, Sudo S & Yagihara S, *J Phys Chem A*, 110 (2006) 4953-4957.