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Effects of PEG plasticizer concentrations and film preparation methods on the structural, dielectric and electrical properties of PEO–PMMA blend based plasticized solid polymer electrolyte films

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Low molecular weight poly(ethylene glycol) (PEG) has been used as plasticizer in the preparation of plasticized solid polymer electrolyte (PSPE) films consisted of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) blend based matrix with lithium tetrafluoroborate ($LiBF_4$) as dopant ionic salt. Solution cast (SC) melt–pressed and the ultrasonic-microwave (US–MW) irradiated solution cast melt–pressed methods have been used for the preparation of these PSPE films. The dielectric dispersion, ac ionic conductivity and structural dynamics of these electrolytes have been studied by employing the dielectric relaxation spectroscopy (DRS) over the frequency range from 20 Hz to 1 MHz, at room temperature. The structural properties of these materials have been characterized by their X–ray diffraction (XRD) measurements. The influence of varying PEG concentrations (5, 10 and 15 wt%) and also the sample preparation methods on the complex dielectric function, ac electrical conductivity, electric modulus and the impedance spectra of these electrolytes have been explored. The ionic conductivity of US–MW prepared PSPE films enhances non-linearly, whereas for the SC prepared films it vary anomalously with the increase of PEG concentrations. The variations in conductivity of these PSPEs are governed by the change in strength of polymer-ion, plasticizer-ion and the polymer-plasticizer interactions and also the polymer chain segmental motion in the solid ion-dipolar complexes. Room temperature ionic conductivity values of the PEG concentrations and sample preparation methods dependent these PSPE electrolytes at low concentration of dopant salt are found in the range from 1.79 to 4.22 μS cm^{-1}, which confirm their suitability in preparation of the all-solid-state ion conducting devices.

Keywords: Solid polymer electrolyte, Dielectric properties, Ionic conductivity, Structural dynamics, X–ray diffraction

1 Introduction

The demand of high performance portable electronic devices and equipments is on an exponential rise in the current decade more than ever. This fact provokes extensive research and development on safer and compact type high energy storing devices based on solid polymer electrolytes (SPEs)[1–7]. The SPE materials exhibit the benefit of various desirable properties such as safety, light weight, high flexibility, mechanical stability, relatively high energy density, multiple charging/discharging cycles and ease of molding in any solid shape and sizes over their previous counter parts of liquid and ceramic electrolytes.

The SPEs have thus become a fascinating area of research in the advanced materials sciences and engineering to meet their apparent technological demands in design and fabrication of rechargeable batteries. The SPEs are basically prepared by complexing the functional groups of polymer/polymers blend with cations of the dopant ionic salt. Various host polymers like poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA), poly(vinyl alcohol) (PVA), poly(vinylidene fluoride) (PVdF), poly(vinyl chloride) (PVC), poly(acrylonitrile) (PAN), poly(vinylidene fluoride-hexafluoro propylene) (PVdF-HFP) etc. have been used so far along with different lithium based alkali salts for the preparation of numerous SPE materials. Among these polymers, PEO is the most commonly used polymer host, endowed with properties like low lattice energy, low glass transition temperature, high solvating power for alkali metal salts and the highly flexible type film forming ability[3,5,6,8–16]. What seems to be the only unfortunate thing is the highly semi-crystalline nature of PEO, which leads to low values of ionic conductivity of its SPEs at ambient temperature, limiting their several useful technological applications. Besides the use of PEO matrix, the PMMA matrix of high amorphicity (more than 96%) is also preferred in preparation of SPE materials because of its light

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*Corresponding author (E-mail: rjsengwa@rediffmail.com) weight, high optical transparency, high strength and dimensional stability[7,17–20]. But the brittle property of PMMA film under a loaded force limits the industrial and technological suitability of its SPEs.

So far, several new strategies have been adopted by the pioneer researchers working in the area of SPE materials to overcome the shortcomings and simultaneously to achieve most of the technological desired properties of the SPEs (high ionic conductivity, suitable film flexibility and better mechanical, thermal and chemical stabilities). These strategies include mixing of plasticizers, addition of inorganic nanofillers and ionic liquids, blending of polymers and altering the preparation methods[21–32]. The PEO–PMMA blend matrix has been recognized as a very good option to overcome the drawbacks of its pristine polymers, as the addition of PEO in PMMA matrix works as plasticizer resulting in increase of PMMA flexibility and thereby reduces the film brittleness, whereas the PMMA environment in PEO matrix increases its amorphous phase[33]. These facts lead to increase in ionic conductivity of the PEO–PMMA blend based SPE films[22–32].

In the Li^+ ion containing PEO matrix based solid complexes, there is a dominant probability that either three or six EO segments (ether oxygen atoms) interact within the first coordination shell of Li^+ ions[23,29]. In case of PMMA based solid ion-dipolar complexes, Li^+ ion mostly coordinates with carbonyl groups (C=O) of the polymer chain backbone units[7,18]. Therefore, in PEO–PMMA blend based electrolytes, formation of such triad and sextant ion-dipolar conformers on the polymer blend chains are also expected by an interplay of both the PEO-ion ($O\cdots Li^+$) and PMMA-ion ($C=O\cdots Li^+$) interactions. Further, addition of plasticizer in SPEs is also very effective structural modification approach which improves the ions mobility and structural dynamics of the solid complexes[13–16]. A plasticizer mainly enhances the amorphicity of crystalline polymer matrix and as a result of this effect, there is increase in ionic conductivity of the plasticized solid polymer electrolyte (PSPE) materials[13–16,20,28–31].

Mostly, non-volatile type low molecular weight and high dielectric constant dipolar liquids such as poly(ethylene glycol) (PEG), ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), γ-butyrolactone (BL) etc. are used as plasticizer in preparation of PSPE films. Thus, blending of polymers and the addition of plasticizer play important roles in the development of new novel PSPEs by fine tuning of their physico-chemical properties along with enhanced ionic conductivity. PEG molecules have hydroxyl groups at the ends of its molecular chains and ether oxygen atoms in the chain backbone owing to which, intra- and inter-molecular hydrogen bonding occurs in the pure PEG[34]. When PEG is added in the polymer-ion complexes, then its H-bonding behaviour modifies the pristine polymer-ion interactions due to formation of polymer-PEG and PEG-ion interactions[26,29,30]. Such modifications in solid ion-dipolar complexes can alter the polymer segmental dynamics and simultaneously the ions transport process. Besides, in general, the ion motion in polymer electrolytes has been shown to result from a combination of intra- and inter-chain hops within a complex coordination structure wherein the Li^+ cations are complexed by multiple segments of the polymer matrix. The variation in preparation methods (solution cast, melt press, ultrasonic and microwave-irradiation, ion-irradiation, ball milling etc.) also play critical role in modification of the SPEs structures and their ionic conductivity at room temperature[10,35,36].

In the present paper, the effects of varying concentrations of plasticizer (PEG) and the film preparation methods on the dielectric and electrical properties, and also the structural properties of the PSPE films have been investigated using dielectric relaxation spectroscopy (DRS) and X–ray diffraction (XRD) techniques, respectively. DRS is a powerful technique for the characterization of polymer segmental motion and ion transportation mechanism in SPE materials besides the study of their dielectric and conductivity dispersion behaviour[7–13]. The new PSPE films consisted of PEO–PMMA blend as host matrix, lithium tetrafluoroborate ($LiBF_4$) as ionic salt and PEG as plasticizer have been prepared by classical solution cast (SC) melt–pressed and ultrasonic assisted followed by microwave irradiated solution cast (US–MW) melt–pressed methods. The choice of PEG used as plasticizer in the preparation of PSPEs is because of its linear chain molecular structure having the same chain backbone units ($–CH_2–CH_2–O–$) as that of the PEO macromolecules, and therefore its use as plasticizer in the present study is interesting from the polymer and plasticizer structural point of view. The main aim of the study is to explore the dielectric, electrical and structural properties of the new composition based PSPE films from their technological application point of view and also from academic interest.

2 Experimental

2.1 Sample preparation

The PEO (M_w = 6×10^5 g mol^{-1}), PMMA (M_w = 3.5×10^5 g mol^{-1}), PEG (M_w = 200 g mol^{-1}) and $LiBF_4$ were obtained from Sigma–Aldrich, USA. The anhydrous acetonitrile and tetrahydrofuran of spectroscopic grade were purchased from Loba Chemie, India. Equal weight amounts of PEO and PMMA, and the required amount of $LiBF_4$ for average molar ratio (EO+(C=O)):Li^+ = 16:1 were used along with the amount of x wt% PEG concentrations (x = 5, 10 and 15 weight amounts with respect to the amount of polymer blend) for the preparation of (PEO–PMMA)–$LiBF_4$–x wt% PEG films by different methods.

The PSPE films were prepared by two different methods namely; classical solution cast (SC) method and the ultrasonic (US) assisted followed by microwave (MW) irradiated solution casting (US–MW) method. Initially, for sample preparation, 1 g each of PEO and PMMA were dissolved in acetonitrile and tetrahydrofuran, respectively, in separate conical flasks. Subsequently, $LiBF_4$ (0.193 g) was added in PEO solution, and it was dissolved and mixed homogenously with the help of a magnetic stirrer. The PMMA solution was then added to this PEO electrolyte solution and again mixed homogeneously, resulting in the (PEO–PMMA) blend based electrolyte solution. After this, x = 5 wt% PEG was added into the electrolyte solution and mixed homogeneously by magnetic stirring to get the plasticized polymeric electrolyte solution. Similar steps were used for preparation of other electrolyte solutions of x = 10 and 15 wt% PEG concentrations.

These plasticized polymeric electrolyte solutions were divided into two equal parts; casting first parts of each directly onto Teflon petri dishes which produced stable and free standing the solution cast (SC) prepared (PEO–PMMA)–$LiBF_4$–x wt% PEG films after evaporation of solvents at room temperature. The second parts of each electrolyte solution were sonicated by using an ultrasonicator (250 W power, 25 kHz frequency) for 10 min duration with ON–OFF step of 15 s. This was done by immersing a stainless steel sonotrode directly into the electrolyte solution for strong dose of the ultrasound. After this, the solutions were irradiated by microwave electromagnetic energy in a domestic microwave oven (600 W power, 2.45 GHz frequency) for 2 min duration and 10 s irradiation step with intermediate cooling. These solutions were designated as ultrasonic and microwave (US–MW) irradiated solutions and same were casted onto petri dishes which result the US–MW prepared PSPE films after solvents evaporation. The surfaces of the prepared electrolyte films were found slightly uneven at micro scale level. To smooth out the surfaces of these films, melt–pressed technique had been used. In this technique, each electrolyte film was initially vacuum dried at 40 °C for 24 h and after that it was melted by heating it up to 130 °C in circular stainless steel die with suitable spacer using polymer film making unit. The melted material was pressed under 2 tons of pressure per unit area and cooled slowly up to room temperature resulting in smooth surfaces of the PSPE film.

2.2 Characterizations

2.2.1 Structural characterization

The structural studies of the PSPE films prepared by both the methods were performed at room temperature using a X–ray diffractometer (PANalytical X′pert Pro MPD powder diffractometer with Cu Kα radiation of wavelength λ = 1.5406 Å operated at 45 kV and 40 mA) in the range $10° \leq 2\theta \leq 30°$ at scanned speed of 0.05°/s. The selection of this small range for the XRD patterns is owing to the fact that most of the prominent reflections of the constituents of these PSPEs fall in the range of above mentioned 2θ values.

2.2.2 Dielectric and electrical characterization

The DRS of the PSPE films was carried out using Agilent technologies 4284A precision LCR meter along with Agilent 16451B solid dielectric test fixture in the frequency range from 20 Hz to 1 MHz for their dielectric and electrical characterization. Prior the sample measurement, the open circuit calibration of the cell was performed to eliminate the effect of stray capacitance of the cell leads. After that, the frequency dependent values of capacitance C_p, resistance R_p and loss tangent ($\tan\delta = \varepsilon''/\varepsilon'$) of each PSPE film sandwiched between the electrodes of the dielectric cell were measured in the parallel circuit operation. Using the measured values of C_p, R_p and tanδ, the spectra of complex dielectric function $\varepsilon^*(\omega) = \varepsilon' - j\varepsilon''$, real part of alternating current (ac) electrical conductivity $\sigma' = \omega\varepsilon_0\varepsilon''$, electric modulus $M^*(\omega) = M' + jM''$ and the complex impedance $Z^*(\omega) = Z' - jZ''$ of the PSPE films were calculated from the expressions described in detail elsewhere[7]. These complex quantities are alternative representations of same macroscopic relaxation data and can be easily transformed to each other according to the scheme $1/\varepsilon^*(\omega) = M^*(\omega) = j\omega C_0 Z^*(\omega) = j\omega\varepsilon_0/\sigma^*(\omega)$, where $\omega = 2\pi f$ is an angular frequency of electric field, ε_0 (8.85 pF m^{-1}) is the permittivity of free space and C_0 is the capacitance of empty test fixture.

3 Results and Discussion

3.1 Structural analysis

The measurement of X–ray diffraction pattern of a material is helpful in structural evaluation with the determination of parameters namely basal spacing, crystallite size, crystalline phase etc. by analyzing the peaks positions, peaks intensities and their widths. The XRD patterns of $LiBF_4$ powder, PMMA, PEO and PEO–PMMA blend films, and the (PEO–PMMA)–$LiBF_4$–x wt% PEG electrolyte films prepared by SC and US–MW methods are shown in Fig. 1(a) and (b), respectively. The PEO peaks positions 2θ and corresponding intensities I and broadening of peaks at half height β for the PSPE films are determined by X'pert pro® software and these are given in Table 1. The values of basal spacing (inter-planar spacing of PEO crystallites) d are determined by Bragg's relation $\lambda = 2d \sin\theta$. The mean crystallite size (length) L in the direction perpendicular to hkl plane of PEO is evaluated by the Scherrer's equation $L = 0.94\lambda/\beta\cos\theta$, where β is in radians. The obtained values of d and L for the studied PSPE films are included in Table 1. Figure 1(a) shows that the XRD pattern for $LiBF_4$ have intense characteristic peak at 26.33°, and some others of relatively low intensities confirming its crystalline nature. The pristine semicrystalline PEO film exhibits two sharp diffraction peaks at $2\theta = 19.22°$ and $23.41°$, which are corresponding to crystal reflection planes 120 and concerted 112,032, respectively, and these are characteristic peaks of PEO[10]. The symmetrical ordering of polyether chains is responsible for the formation of such type of crystalline nature in pristine PEO structures. Figure 1 shows that the pristine PMMA film has a broad and diffused peak around 16°, which confirms its predominantly amorphous phase[7]. The blend of PEO–PMMA also have the PEO diffraction peaks but these are of relatively low intensities as compared to pristine PEO peaks which confirms the decrease of crystalline phase of PEO when it is blended with amorphous PMMA. A correlation between the intensity (height) of the peak and the degree of crystallinity of the semicrystalline polymeric films has already been established[37,38].

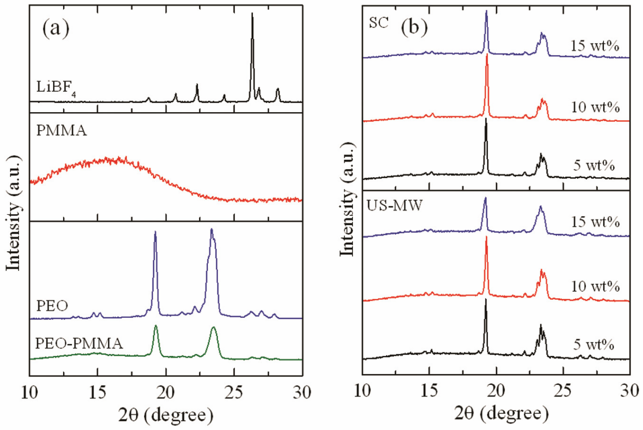

Fig. 1 – XRD patterns of (a) $LiBF_4$ powder, PMMA, PEO, and PEO–PMMA blend films, and; (b) (PEO–PMMA)–$LiBF_4$–x wt% PEG electrolyte films prepared by SC and US–MW methods

The XRD patterns of the PSPE films (Fig. 1(b)) show that peaks corresponding to $LiBF_4$ are not observed in any of the polymer-salt complexes which signify solvation of salt into the blend matrix. The reason behind it is the formation of large range ion-dipolar complexes of cations with the functional groups of PEO–PMMA blend and the polar groups of PEG plasticizer, which prevents the crystallization of PEO and an increased amount of amorphous phase is produced in these PSPE materials. Table 1 shows that there is an insignificant variation in d values with the increase of PEG concentration and also the change in PSPE preparation methods. Figure 2 shows that the values of crystallite sizes L decrease on increase of PEG concentration suggesting the enhancement in the degree of disorder in the PSPE complexes. Due to the structural disordering number of small size crystallites spread throughout the material reduce and result in formation of some scattered bigger size crystallite domains. The I values of 120 peak of SC prepared PSPE films (Table 1) are found higher than that of the PEO–PMMA blend film peak intensity (4746 counts), whereas the 112,032 reflection peak intensities of PSPE films significantly reduces as compared to that of the PEO–PMMA blend peak (4800 counts), which reveals that the overall degree of amorphous phase of electrolyte films have increased as compared to the amorphicity amount of the pristine polymer blend. Further, comparison of I values reveals that the degree of amorphicity of the US–MW prepared films are relatively high as compared to that of the SC prepared PSPE films of same PEG concentration. These values

Table 1 — Values of Bragg’s angle 2θ, basal spacing *d*, broadening of peak at half height β, mean crystallite size *L* and intensity *I* of diffraction peaks in (PEO–PMMA)–$LiBF_4$–*x* wt% PEG electrolyte films prepared by SC and US–MW methods

x wt% PEG	2θ (°)	*d* (nm)	β (radians)	*L* (nm)	*I* (counts)
			120 reflection peak parameters of PEO		
SC method					
5	19.23	0.461	0.0030	49.50	6806
10	19.31	0.459	0.0032	45.59	7859
15	19.27	0.460	0.0034	43.60	5445
US–MW method					
5	19.22	0.461	0.0028	51.94	4756
10	19.27	0.460	0.0032	45.98	5333
15	19.17	0.462	0.0050	29.52	3275
			112,032 reflection peak parameters of PEO		
SC method					
5	23.34	0.381	0.0086	17.29	2690
10	23.43	0.379	0.0091	16.32	2486
15	23.39	0.380	0.0092	15.80	2794
US–MW method					
5	23.33	0.381	0.0082	18.14	2852
10	23.38	0.380	0.0091	16.26	2607
15	23.31	0.381	0.0115	12.89	2572

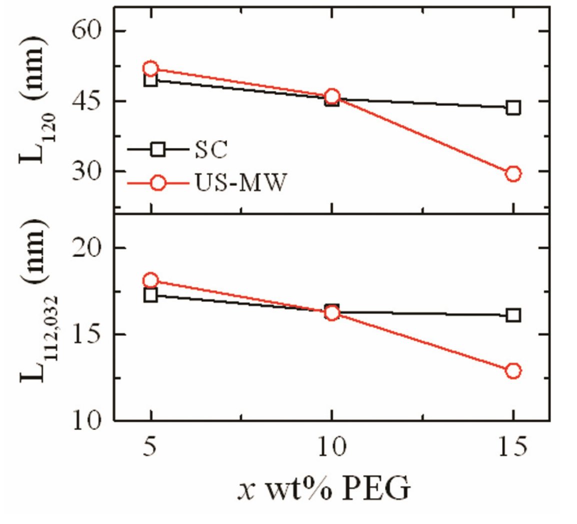

Fig. 2 – PEG concentration dependent values of the mean crystallite size *L* of (PEO–PMMA)–$LiBF_4$–*x* wt% PEG electrolyte films prepared by SC and US–MW methods

also infer that the degree of crystalline phase of PSPE films vary anomalously both with their preparation method and also with the increase of PEG concentration. Further, the low values of 120 reflection plane intensity of the PSPE films prepared by US–MW method as compared to the SC method prepared films confirm that the ultrasonication and microwave irradiation treatments disturb the degree of crystalline structures relatively more in these solid ion-dipolar complexes.

3.2 Dielectric spectra

The frequency dependent complex permittivity (real part ε′ and dielectric loss part ε″) spectra of (PEO–PMMA)–$LiBF_4$–*x* wt% PEG electrolyte films prepared through SC and US–MW processes are shown in Fig. 3(a) and (b), respectively. The ε′ values of these electrolytes are very high (~10^4 to 10^5) at lower end of the spectra and these values decrease linearly with increase of frequency up to 10 kHz (on log-log scale). This dispersion behaviour of ε′ values reveals the dominant contribution of the electrode polarization (EP) effect in the bulk properties over low frequency region which is common characteristic of SPE materials[10–13]. Around 10 kHz, these ε′ plots exhibit point of inflexion. These ε′ values decrease non-linearly with increasing frequency above 10 kHz attributed to dipolar polarization of these PSPEs which finally approach the steady state (high frequency limiting permittivity, ε_∞) near 1 MHz as shown in inset of the figure. The ε_∞ values are mainly a measure of rapid polarization of atoms and electrons due to the application of a time dependent electric field on a dielectric material. The ε_∞ values of these electrolyte films at room temperature are recorded in Table 2, which are around 10. Generally, the ε_∞ values for pristine polymers are around 2, but much higher ε_∞ values of PSPEs are owing to the presence of ions and high static permittivity (ε_s = 19.69 at 25 °C) of dipolar PEG[34] in the PEO–PMMA blend matrix. The ε_∞ values of the PSPE films prepared by SC method vary anomalously with the increase of PEG concentration, whereas an increase in ε_∞ values is observed for the US–MW method prepared PSPE films with increase in concentrations of PEG (Table 2). These results suggest that the inclusion of PEG concentration in the polymer blend matrix have altered localization of charge carriers including mobile Li^+ ions with change of PSPE preparation methods. So it is quite evident that the PEG concentration plays significant role in the strength of ion-dipolar interactions and the dipolar ordering which influences the localization of charge carriers.

The ε'' values of the PSPEs have a linear decrease over the broad frequency range having slope $m = -0.9$ (on log-log scale) with a small deviation at higher end of spectra (see inset of Fig. 3). It is further observed that no distinct relaxation peak is observed in the ε'' spectra confirming that the dominant contribution of ionic conductivity suppresses such peak in these PSPEs. It is found that the ε'' values at low frequencies are slightly higher than the corresponding ε' values of the PSPE films. Further, these ε'' values also vary anomalously with increase of PEG concentration in the PSPEs. These comparative results reveal that the dielectric properties of these PSPEs are anomalously

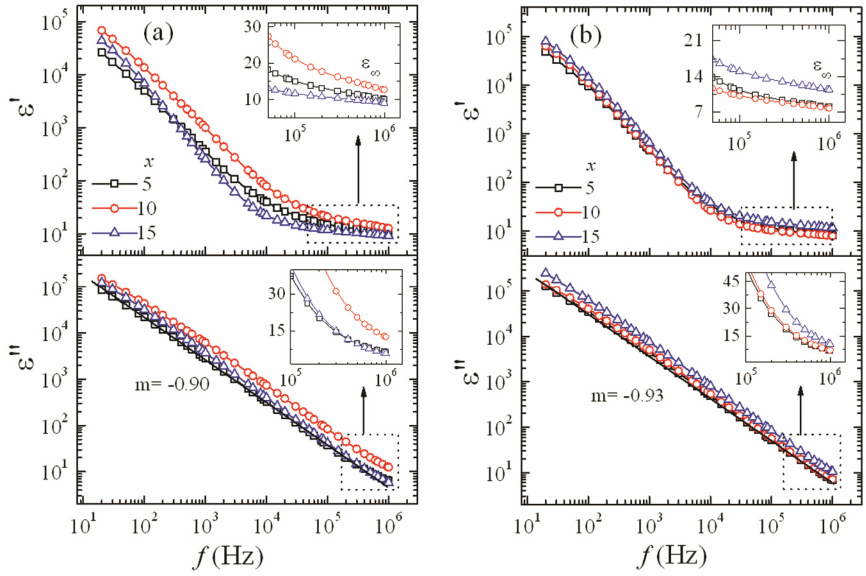

Fig. 3 – Frequency dependent real part ε' and loss part ε'' of the complex dielectric function of (PEO–PMMA)–$LiBF_4$–x wt% PEG electrolyte films prepared by (a) SC and (b) US–MW methods. Insets show the enlarged view of the spectra in high frequency region

Table 2 — Room temperature values of high frequency limiting permittivity ε_∞, polymer segmental motion relaxation time τ_s, impedance relaxation time τ_z, modulus relaxation time τ_M, dc ionic conductivity σ_{dc} ($\sigma_{dc}(R_b)$ determined from impedance plots and $\sigma_{dc}(\sigma')$ determined from power law fit of σ' spectra) and fractional exponent n of (PEO–PMMA)–$LiBF_4$–x wt% PEG electrolyte films prepared by SC and US–MW methods

x wt% PEG	ε_∞	τ_s (μs)	τ_z (μs)	τ_M (μs)	$\sigma_{dc}(R_b)\times10^6$ (S cm^{-1})	$\sigma_{dc}(\sigma')\times10^6$ (S cm^{-1})	n
SC method							
5	10.17	47.00	0.61	0.26	1.74	1.79	0.85
10	12.70	17.00	0.33	0.13	4.10	4.22	0.88
15	9.13	36.40	0.41	0.22	2.15	2.20	0.81
US–MW method							
5	7.83	26.50	0.28	0.19	2.68	2.55	0.68
10	8.09	20.90	0.26	0.17	2.99	2.86	0.55
15	11.42	19.90	0.25	0.13	4.43	4.18	0.53

influenced by PEG plasticizer concentrations and the sample preparation methods.

3.3 Conductivity spectra

Figure 4(a) and (b) illustrates the frequency dependent ac ionic conductivity σ′ and the dielectric loss tangent tanδ spectra of (PEO–PMMA)–$LiBF_4$–*x* wt% PEG electrolytes prepared by SC and US–MW methods, respectively. There is a non-linear increase by about one order of magnitude in σ′ values of the PSPE films with increase of frequency from 20 Hz to 1 MHz. Similar to the other SPE materials[10,11,29,30], the σ′ spectra are characterized by three different regions spreading over the entire frequency range; first (I) is the low frequency region with dominating contribution of EP effect, second (II) is the dc plateau region in the intermediate frequency range which represents the long–time ion dynamics or the ‘diffusive dynamics’ characterized by random walks, and the third (III) region at higher frequencies is the ac dispersive region resulting due to the short–time ion dynamics or the ‘subdiffusive dynamics’ characterized by back–and–forth motion over the limited range. The frequency at which dc to ac dispersion starts is known as hopping crossover frequency. The jumps of ions between different ion coordination sites of polymer matrix through hopping mechanism are demonstrated by random barrier model which consequences the ac conductivity dispersion at higher frequencies in the SPEs and other ion conducting disordered materials[39].

The log-log plot of ac conductivity in the intermediate and high frequency region (II and III) of these PSPEs follows the power law behaviour, and hence the values of dc ionic conductivity σ_{dc} are determined by fitting the σ′ spectra to the Jonscher’s power law[40] $\sigma'(\omega) = \sigma_{dc} + A\omega^n$, where A is the pre–exponential factor and n is the fractional exponent having values between 0 and 1. These fits data are shown by solid lines along with the experimental values points in the σ′ spectra. The observed values of σ_{dc} (denoted by $\sigma_{dc}(\sigma')$) and n of the PSPEs with varying PEG concentrations are given in Table 2. The n values of these electrolytes are found in the range from 0.53 to 0.88, suggesting hopping mechanism of ion transportation as reported in earlier studies on SPE materials[10,11,38]. In this type of ion transportation mechanism, when an ion hopping takes place from one coordination site to another in the ion-dipolar complexes, the originally occupied site will relax and the new site will deform to accommodate the incoming ion, and in such process ions motion is expected to be coupled with the polymer chain segmental dynamics[39–41].

It is noticeable from Table 2 that the σ_{dc} values of (PEO–PMMA)–$LiBF_4$–*x* wt% PEG electrolytes increase from 2.55 μS cm^{-1} to 4.18 μS cm^{-1} with increase of PEG concentration from 5 to 15 wt% for the US–MW method prepared PSPE films. But in case of SC method prepared PSPE films, the σ_{dc}

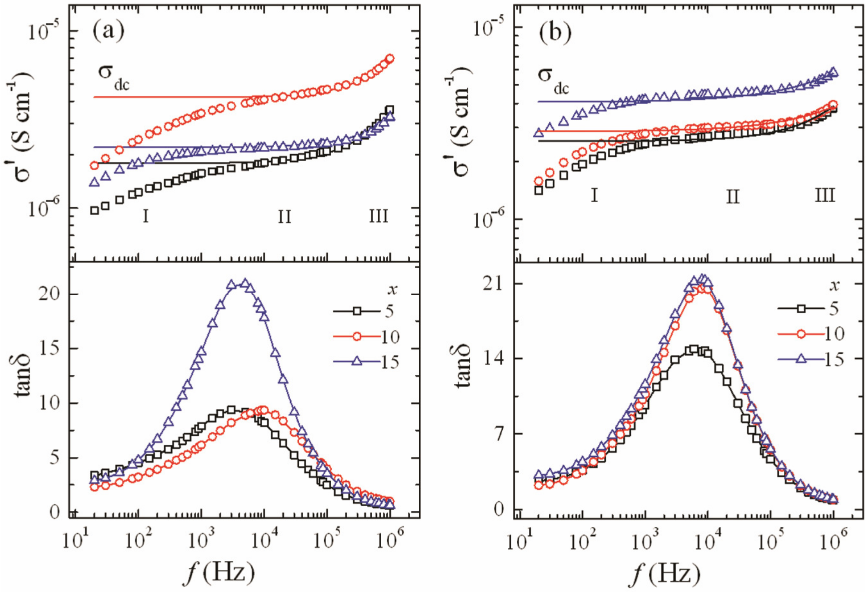

Fig. 4 – Frequency dependent real part of ac conductivity σ′ and loss tangent (tanδ) of (PEO–PMMA)–$LiBF_4$–*x* wt% PEG electrolyte films prepared by (a) SC and (b) US–MW methods. Solid lines represent the Jonscher’s power law fit of the experimental data. I, II and III are the different regions of low, intermediate and high frequencies where ions have different type of transportation behaviour

values increase anomalously with PEG concentrations and found maximum 4.22 μS cm^{-1} for 10 wt% PEG containing PSPE film which is approximately two times higher than that of the σ_{dc} values 1.79 μS cm^{-1} and 2.20 μS cm^{-1} of 5 and 15 wt% PEG containing films, respectively. The increase in σ_{dc} values is attributed to the increased mobility of the ions which is influenced by several factors in the solid polymer-ion complexes. Earlier[29], in our laboratory, the conductivity study on (PEO–PMMA)–$LiCF_3SO_3$–x wt% PEG electrolytes also revealed a small variation in their σ_{dc} values with increase of PEG concentration from 5 to 15 wt%. Further, the conductivity study on PEO–$LiCF_3SO_3$–x wt% PEG electrolytes confirmed that there is a small increase of σ_{dc} values with increase of PEG concentrations from 5 to 15 wt% and it decreases significantly on addition of 20 wt% PEG concentration[16]. The small effect on the σ_{dc} enhancement by PEG plasticizer may be owing to the same repeat units of PEO and PEG chains backbones. The correlation of conductivity values with polymer segmental dynamics for these PSPE films are discussed later in a separate section.

The Debye type relaxation peaks are exhibited in tanδ spectra of the investigated PSPE films (Fig. 4(a) and (b)). It is clearly seen that the frequency value corresponding to tanδ peak is coinciding with the starting frequency of the dc plateau region of σ' spectra for each PSPE film. Besides the fact that the PMMA monomer unit is much bulkier than the PEO monomer unit, the appeared single peak in tanδ spectra suggests the cooperative polymer segmental dynamics of both the polymers in the ion-dipolar complexes of these PSPE electrolytes. The varying concentration of PEG and the sample preparation methods affect the magnitude of tanδ peaks too as can be seen in the figures. It is found that 15 wt% PEG sample has much higher loss tangent among the SC prepared PSPE films, whereas 10 and 15 wt% PEG samples have relatively higher loss tangent values for US–MW prepared PSPE films.

The relaxation time τ_s values of cooperative chains segmental motion in the complexed structures are determined by the relation $\tau_s = 1/2\pi f_{p(\tan\delta)}$, where $f_{p(\tan\delta)}$ is the frequency value corresponding to tanδ peak. The τ_s values of the PSPEs prepared by both SC and US–MW methods at various concentration of PEG are given in Table 2. Among the various films prepared by SC method, the τ_s value is lowest for the 10 wt% PEG film, explaining the fast segmental dynamics in this sample and hence its ionic conductivity is relatively high. But in case of US–MW method prepared PSPE films, the τ_s values are non-linearly decreasing with increase of PEG concentration confirming enhancement in polymer segmental dynamics of the complexed structures owing to which σ_{dc} values also increase non-linearly. Further, it is found that the τ_s value of US–MW method prepared PSPEs are lower as compared to that of the SC method prepared electrolyte films (except 10 wt% PEG sample), which explain their corresponding higher conductivities. The inverse correlation between σ_{dc} and τ_s values of SPE materials have been reported in several investigations[10–12]. Furthermore, the observed σ_{dc} values of the PEO–PMMA blend based PSPEs at room temperature are of the order of μS cm^{-1} confirming them as potential candidates for their use in preparation of various ion conducting devices.

3.4 Electric modulus spectra

The electric modulus spectra are studied for these PSPEs due to the very fact that they are free from the contribution of EP effect, independent of the nature of electrode material and the electrode/dielectric specimen contact, and also the adsorbed impurities in the sample[7,10–13,41–43]. Figure 5 (a) and (b) shows the electric modulus (real part M' and loss part M'') spectra of the (PEO–PMMA)–$LiBF_4$–x wt% PEG electrolyte films prepared by SC and US–MW methods. The M'' spectra of these PSPEs have dispersion above 10 kHz, whereas in the EP effect dominated frequency region their values are found close to zero because of the product $M^*(\omega)\cdot\varepsilon^*(\omega) = 1$. Mostly, the M'' spectra of the ion conducting electrolytes exhibit a relaxation peak in high frequency region corresponding to the ionic conductivity relaxation time[10,11,26,41–43], but these peaks seem to appear close to upper frequency limit of our experimental range for 5 and 10 wt% PEG films, and but for 15 wt% PEG film the conductivity relaxation peak is clearly exhibited around 600 kHz for SC method prepared film. The M'' peaks frequency values of the PSPEs were estimated by polynomial fit of the experimental data as shown by solid lines in the figure. The frequency values were used to determine the modulus relaxation time τ_M (also known as conductivity relaxation time τ_σ) in the relation $\tau_M = 1/2\pi f_{p(M)}$, where $f_{p(M)}$ is the frequency corresponding to M'' peak. The observed τ_M values of these PSPEs are given in Table 2. The correlation between τ_M and σ_{dc} values of these PSPE films has also been observed. For lower τ_M, the σ_{dc} value is higher and vice-versa. The τ_M values are attributed to ion mobility for these PSPEs. These τ_M values have direct correlation with τ_s values which reveals that the PSPE films which have higher segmental motion also have relatively high ion mobility in solid ion-dipolar complexes.

3.5 Impedance spectra

The impedance spectroscopy is used for the study of dc ionic conductivity and to separate the EP effect dominated frequency region and the bulk properties frequency region[10,11]. Figure 6(a) and (b) represents the frequency dependent variation of complex impedance (real part Z' and reactive part Z'') of the PSPEs prepared by SC and US–MW methods, respectively. On log-log scale, the Z' values show a slow decrease with increase of frequency in the low and up to intermediate frequency regions, whereas in the high frequency region it decreases sharply. It is found that the behaviour of Z' is inverse of the σ' value at fixed frequency, i.e., for low Z', the σ' value is high and

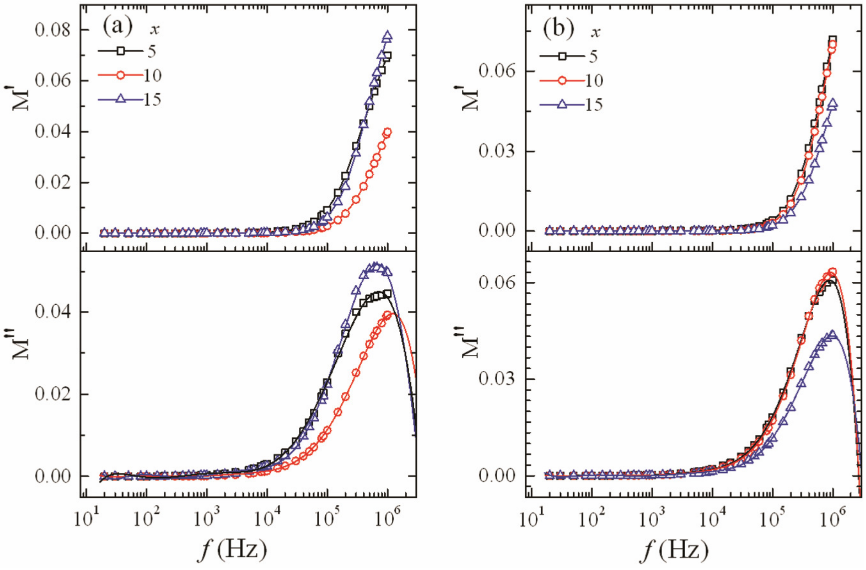

Fig. 5 – Frequency dependent real part M' and loss part M'' of complex electric modulus of (PEO–PMMA)–LiBF$_4$–x wt% PEG electrolyte films prepared by (a) SC and (b) US–MW methods

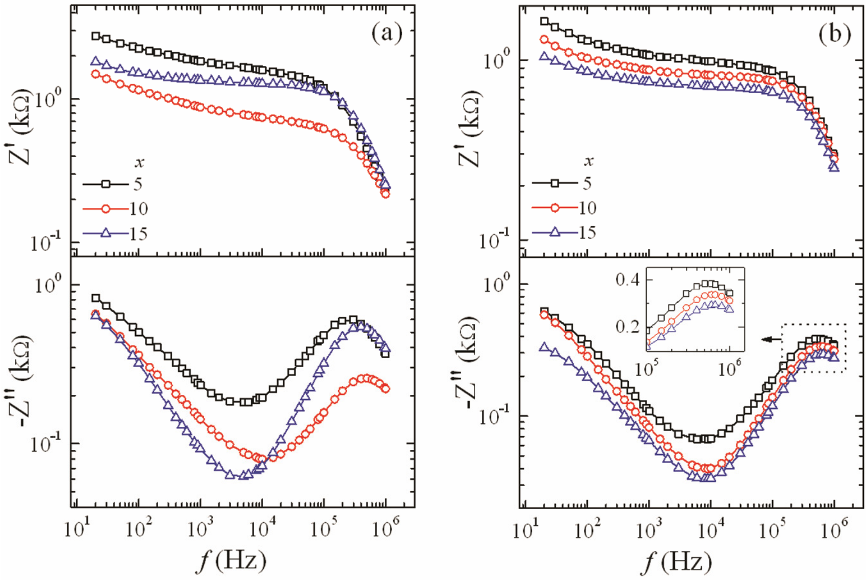

Fig. 6 – Frequency dependent real part Z' and reactive part Z'' of the complex impedance of (PEO–PMMA)–LiBF$_4$–x wt% PEG electrolyte films prepared by (a) SC and (b) US–MW methods. Inset shows the enlarged view of Z'' at high frequencies

vice-versa. The Z'' spectra in the beginning show a large decrease with increase of frequency and approach a minimum value in the mid frequency region. The frequency value corresponding to minimum in Z'' spectra is found same as that of the peak frequency of tanδ spectra. Above these minimums, the values increase and exhibit impedance relaxation peak in high frequency region which is slightly at lower frequency side as compared to the modulus relaxation frequency. Therefore, these relaxation peak values could also be used to analyze the correlation between relaxation time and ionic conductivity values. The values of impedance relaxation time τ_z were determined using the frequency $f_{p(z)}$ values corresponding to the Z'' peaks in the expression $\tau_z = 1/2\pi f_{p(z)}$, and the observed values are recorded in Table 2. The τ_z values are found nearly two orders of magnitude lower than that of the corresponding τ_s values of these PSPE materials. A comparison in variation of τ_z and σ_{dc} values also confirms the correlation between these parameters. Results suggest that as the τ_z decreases, the σ_{dc} value increases and vice-versa.

The Nyquist impedance plots (Z''vs Z') of the PSPE films prepared by SC and US–MW methods are depicted in Fig. 7(a) and (b), respectively. In these plots the frequency values increase on going from right to left side of the plot. These plots are used for determination of bulk dc resistance R_b and from it the dc ionic conductivity of the PSPE material. This is common technique used for the evaluation of σ_{dc} values of various SPEs[10,44–47]. Further, these plots are very useful in evolution of equivalent circuits of the SPE materials which comprises a parallel combination of bulk resistance R_b and geometrical capacitance C_g of the sample in series with a constant phase element (CPE) that consists of a double layer interfacial capacitance and a charge transfer resistance[14,48]. The spike exhibited in the low frequency impedance values attribute to the EP dominated part and a semicircular type arc in the high frequency region represents the bulk properties of the SPEs. The spikes of these spectra are not parallel to the imaginary axis, as in case of ideal capacitive element, which are owing to some irregularities at the electrode /electrolyte contact. The bulk resistance R_b values of the PSPE films are determined by the common intercept of the arc and the spike line on the real axis which are marked in the figure. The frequency corresponding to the intercept point separates the bulk and EP affected frequency regions of the electrolyte material. The σ_{dc} values of the PSPE films were also determined from R_b values using the relation $\sigma_{dc} = t_g/R_bA$, where t_g is the thickness and A is the surface area of the film. These observed σ_{dc} values are denoted by $\sigma_{dc}(R_b)$ in Table 2. The σ_{dc} values of the PSPE films determined by both the power law fit and using R_b value are found almost same (Table 2), which reveals that both the techniques are suitable in determination of σ_{dc} value, but the n value obtained from power law gives additional information regarding the behaviour of ion transportation mechanism, which is hopping type for the investigated PSPE films.

3.6 Correlation between ionic conductivity and various relaxation times

The variation of τ_s, τ_z, τ_M and σ_{dc} values with the varying concentration of PEG for PSPE films prepared by SC and US–MW methods is shown in Fig. 8. This plot is correlating the dc ionic conductivity with the various relaxation times determined from the loss spectra of different complex quantities of these PSPEs. From figure, it is clearly

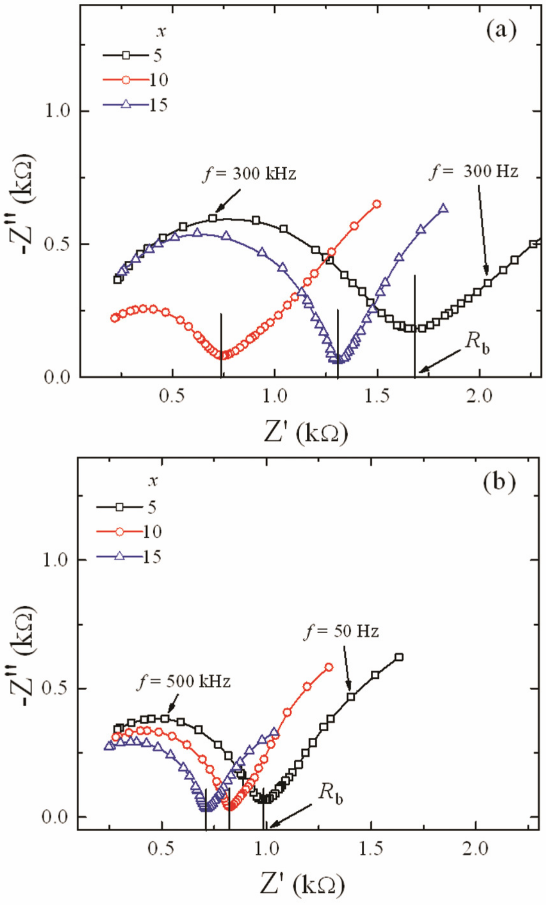

Fig. 7 – Complex impedance plane plots (Z'' vs Z') of (PEO–PMMA)–LiBF$_4$–x wt% PEG electrolyte films prepared by (a) SC and (b) US–MW methods

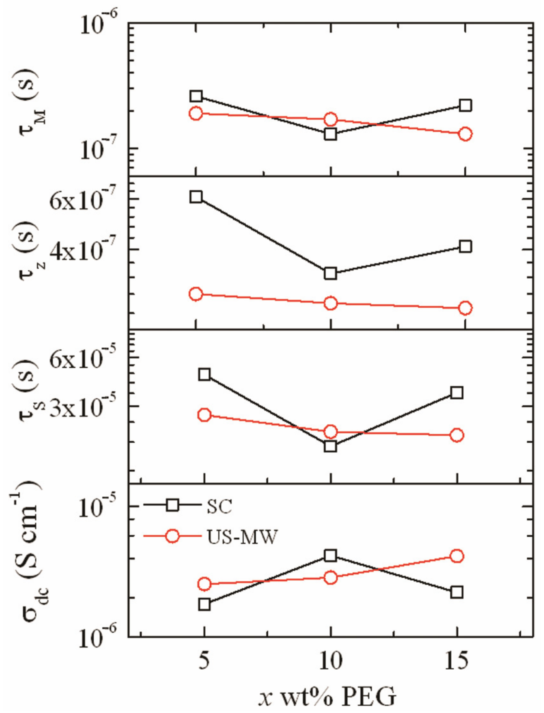

Fig. 8 – PEG concentration dependent modulus relaxation time τ_M, impedance relaxation time τ_z, loss tangent relaxation time τ_s and dc ionic conductivity σ_{dc} of (PEO–PMMA)–LiBF$_4$–x wt% PEG electrolyte films prepared by SC and US–MW methods

seen that the σ_{dc} value of US–MW method prepared films increase gradually with the increase of PEG concentration, and the values of various relaxation times decrease. These results favour the fact that the transportation of ions occur coupled with polymer chain segmental dynamics in which enhancement of segmental dynamics (τ_s) enhances the ions mobility (τ_M) in the faster relaxing impedance media (τ_z). In case of SC method prepared PSPEs, 10 wt% PEG has the highest dc ionic conductivity which is favoured by the fast polymer segmental dynamics as revealed from the observed lowest values of τ_s and τ_z. The non-linear increase in ionic conductivity of the US–MW electrolyte films, even at 15 wt% PEG owes to their treatment with high intensity ultrasonication, whereas, the higher percentage addition of PEG in SC method prepared PSPEs has lead to lowering of ionic conductivity due to increment of relaxation times (Fig. 8). These results clearly infer that the variation in strength of various kind of interactions in the investigated PSPE films resulted in either lowering or enhancing of the polymer segmental dynamics, the ions mobility and impedance relaxation and according to which ionic conductivity changed. Further from these results it can be concluded that determination of any of the relaxation time is suitable in explanation of conductivity variation with the change in composition of the PSPE films, although these dynamic processes occurs at different time scales.

4 Conclusions

The structural, dielectric and electrical properties of the (PEO–PMMA)–LiBF$_4$–x wt% PEG electrolytes prepared by SC and US–MW methods were studied and analyzed in detail in the present paper. The XRD patterns and the structural parameters reveal that the amorphous phase vary anomalously with the increase of PEG concentration and also the sample preparation methods of these PSPE films. The dielectric and electrical properties of the PSPEs are observed to be largely dependent on the sample preparation methods and the PEG concentrations. The ionic conductivity of PSPE films prepared through US–MW method has increased non-linearly, whereas, for the SC method prepared films, the σ_{dc} values vary anomalously with increase of PEG concentration. The ionic conductivity of these electrolyte films has a correlation with the polymer segmental dynamics, electric modulus and impedance relaxation times whatever is the method used in sample preparation and the concentration of plasticizer added. Results reveal that the ions mobility in the studied PSPE films are owing to cations coordinated polymer chain segmental motion through hopping mechanism. The dc ionic conductivity values of these plasticized PEO–PMMA blend based electrolyte films having low ions concentration are of the order of μS cm^{-1}, which is appealing for their use as electrolytes in fabrication of various ion conducting devices.

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