

Effects of ultrasonic assisted processing and clay nanofiller on dielectric properties and lithium ion transport mechanism of poly(methyl methacrylate) based plasticized polymer electrolytes

Shobhna Choudhary,¹ Adam Bald,² Ram Jeewan Sengwa,¹ Dorota Chęcińska-Majak,² Krzysztof Klimaszewski²

¹Dielectric Research Laboratory, Department of Physics, Jai Narain Vyas University, Jodhpur, Rajasthan 342 005, India

²Department of Physical Chemistry of Solutions, University of Łódź, 90-236 Łódź, Pomorska 163, Poland

Correspondence to: S. Choudhary (E-mail: shobhnachoudhary@rediffmail.com)

ABSTRACT: Lithium ion conducting solid polymer electrolyte (SPE) films consisted of poly(methyl methacrylate) (PMMA) matrix with lithium perchlorate as a dopant ionic salt, poly(ethylene glycol) as plasticizer and montmorillonite clay as inorganic nanofiller have been prepared by classical solution casting and high intensity ultrasonic assisted solution casting methods. The X-ray diffraction study confirmed the amorphous structure of all these PMMA-based solid electrolytes and the clay nanosheets existed in exfoliated form in their amorphous phase. Dielectric relaxation spectroscopy had been employed for the investigation of complex dielectric function, ac electrical conductivity, electric modulus, and impedance spectra of these electrolytes over the frequency range from 20 Hz to 1 MHz. It was observed that the dielectric properties and ionic conductivity of the electrolytes strongly depended on the sample preparation methods, and also had changes with addition of the clay nanofiller. Temperature-dependent dielectric study of the electrolyte films confirmed that their dc ionic conductivity and conductivity relaxation time values obeyed the Arrhenius behavior. This study also revealed that the lithium ion transportation in the ion–dipolar complexes of these electrolytes occurred through hopping mechanism and it was correlated with the conductivity relaxation time. Preparation of these electrolyte films through ultrasonic assisted solution casting method increased the ionic conductivity by more than one order of magnitude in comparison to that of the classical solution casting method, which revealed that the former was a novel method for the preparation of these SPEs of relatively enhanced ionic conductivity. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42188.

KEYWORDS: batteries and fuel cells; clay; composites; dielectric properties; X-ray

Received 13 December 2014; accepted 16 March 2015

DOI: 10.1002/app.42188

INTRODUCTION

In the last one decade, tremendous research work is in progress on the solid polymer electrolytes (SPEs) because of their potential applications in fabrication of high energy storage rechargeable batteries and in the electrochromic devices.^{1–18} The major advantages of SPEs over the liquid and ceramic electrolytes are their light weight, leak proof, easy preparation, high flexibility and compact in size, longer life span with improved safety, and better electrochromical performances. These physico-chemical properties realize the SPE materials as novel in regards to their technological point of view. However, the biggest challenge with the SPE materials is their low ionic conductivity at ambient temperature. To overcome this challenge, the understanding of ion conduction mechanism as well as its enhancement by different processes of the sample preparation is critical.^{2,6,7,18} Recently, authors have confirmed that the high intensity ultraso-

nication and microwave irradiated solution cast prepared SPE films based on poly(ethylene oxide) (PEO) matrix have significant improvement in their ionic conductivity.⁶ Considering this fact, in the present article the ultrasonicated processing method of sample preparation has been applied in order to explore its effect on dielectric behavior and ionic conductivity of plasticized poly(methyl methacrylate) (PMMA) based SPEs.

Mostly, PEO matrix is used for the preparation of SPEs due to its good solvating power for the alkali salts and also the highly flexible type film forming ability.^{2–11,14–16} But high crystallinity of PEO is its major drawback in ion transportation because ions mobility is relatively fast in amorphous phase of polymer matrix. Besides the use of PEO matrix, PMMA is also considered in preparation of the polymeric electrolytes because of its amorphous structure.^{13,18–27} The presence of bulky ester functional group (O=C–O–CH₃) in monomer units results in

flexible behavior of the PMMA chain. The electron donating carbonyl (C=O) functional group of PMMA is highly active for the cations coordination with the alkali metal salts which leads to the formation of broad range ion-dipolar complexes in the solid state. But the major drawback of the electrolyte film based on PMMA matrix is its brittle nature which limits the use of this material in fabrication of flexible type ion conducting solid state devices. To overcome this drawback, PMMA-based SPEs are prepared with the addition of various types of plasticizers and also with the inorganic nanofillers.^{13,21,22,25} The addition of plasticizers increases the SPE film flexibility, amorphous phase, and also the degree of salt dissociation due to which the ionic conductivity of the film increases.^{13,21,22,24,25} The dispersion of inorganic nanofiller increases the thermo-physical properties of the polymeric electrolyte materials in addition to increase of their ionic conductivity.^{21,26,27} The montmorillonite (MMT) clay as inorganic nanofiller is extensively used in the preparation of solid polymeric nanocomposite electrolytes (SPNEs).^{8,20,21,26–29} The investigations on PMMA nanocomposites prepared with MMT nanofiller have established that the presence of exfoliated and intercalated MMT nanosheets in the PMMA matrix improves the thermal, mechanical, gas barrier and corrosion protection properties, and also reduces flammability with a little change in optical transparency of the film.^{30–34} Although, different plasticizers and nanofillers have been used in preparation of PMMA-based electrolytes but the effect of processing technique on ion conduction is merely attempted.

Our survey of literature reveals that fewer attempts have been made to characterize the dielectric dispersion and ion conduction mechanism in PMMA-based electrolyte films containing poly(ethylene glycol) (PEG) as plasticizer and MMT as nanofiller using dielectric relaxation spectroscopy (DRS). The DRS is a highly sensitive spectroscopic technique for the investigation of dielectric strength, relaxation times associated with cations coordinated polymer chain dynamics, and their correlation with ion transportation in the solid polymeric electrolytes.^{4–6,8,10–12,35–38} Recently, we have characterized the dielectric relaxation and ion conduction mechanism in PEO- and PMMA-based SPEs using DRS.^{6,8,28,29,38}

The study on lithium perchlorate (LiClO₄) salt concentration dependent ionic conductivity of solid PMMA–LiClO₄ electrolytes reveals that the optimum limit of salt dissociation in this composition is at 4 : 1 stoichiometric ratio of carbonyl groups (C=O) of PMMA to the lithium cations (Li⁺) of LiClO₄.¹⁹ At higher salt concentration to this stoichiometric ratio, the PMMA–LiClO₄ electrolyte has polymer–salt complexes along with some amount of undissolved salt. Therefore, it is quite interesting to investigate the detailed dielectric properties and relaxation processes of optimum salt concentration PMMA–LiClO₄ electrolytes in presence of MMT as nanofiller and PEG as plasticizer. The use of PEG as plasticizer is appealing due to its wide range inter- and intra-molecular hydrogen bond formation ability.³⁹ The presence of ends hydroxyl groups (–OH) and oxygen atom of ethylene oxide unit (–CH₂–CH₂–O–) in PEG chain can interact with the functional group of polymer, ions of the salt and the silanol groups of MMT. These interac-

tions may alter the polymer segmental dynamics and also the ionic conductivity of the plasticized polymer electrolytes. But the strength of these interactions and the ordering of ion-dipolar coordination in the polymeric electrolytes significantly depend on the material mixing processes.^{2,6,18,29} Therefore, the optimization of material processing and preparation method is very important to achieve the required ionic conductivity at ambient temperature with the detailed structural properties of the SPE materials.

In continuation of our work on SPEs,^{6,8,18,29,35,36,38,40} this article deals with the comparative dielectric dispersion and relaxation behavior study of the PMMA–LiClO₄–10 wt % PEG and PMMA–LiClO₄–10 wt % PEG–5 wt % MMT electrolyte films prepared by two different methods. The stoichiometric ratio (C=O) : Li⁺ = 4 : 1 is used in order to avoid the ion-pairing effect. About 10 wt % concentration of PEG in comparison to weight of PMMA is appropriate in order to reveal the effect of plasticizer on ionic conductivity of the SPE film. Higher concentration of PEG may turn the SPE into gel form, so it is avoided. Mostly, 1–5 wt % concentration of inorganic nanofiller is used in preparation of polymer-based nanocomposite material. Therefore, in the present study 5 wt % concentration of MMT is added for preparation of PMMA-based plasticized nanocomposite electrolyte. This study has been carried out with two main aims. Firstly, to explore the effects of PEG addition and MMT dispersion on the dielectric properties, ionic conductivity and relaxation processes of PMMA-based electrolyte materials. Secondly, it is intended to explore the effect of ultrasonic assisted processing on various dielectric/electrical parameters of the material in order to judge it as a novel method for enhancement of ionic conductivity in the SPEs.

EXPERIMENTAL

Sample Preparation

The PMMA ($M_w = 3.5 \times 10^5$ g/mol), LiClO₄ (battery grade, dry, 99.9% metal basis), PEG ($M_w = 200$ g/mol), MMT clay (Nanoclay, PGV, a product of Nanocor[®]), and tetrahydrofuran were obtained from Sigma-Aldrich, The United States. All the chemicals were vacuum dried before their use in preparation of the SPE films.

The SPE films of PMMA–LiClO₄–10 wt % PEG and PMMA–LiClO₄–10 wt % PEG–5 wt % MMT were prepared by “classical” solution casting (SC) and ultrasonic-assisted processed solution casting (US–SC) methods. Initially, two separate PMMA–LiClO₄ solutions were prepared by dissolving required amounts of PMMA and LiClO₄ [for (C=O) : Li⁺ = 4 : 1 stoichiometric ratio] in tetrahydrofuran. After that 10 wt % concentration of PEG was added in each of the solution which resulted in PMMA–LiClO₄–10 wt % PEG electrolyte solutions. In one of the solutions 5 wt % concentration of MMT with respect to the weight of dissolved PMMA was added to form the PMMA–LiClO₄–10 wt % PEG–5 wt % MMT electrolyte solution. Subsequently, each solution was homogeneously mixed by vigorous magnetic stirring. After that each homogeneously mixed solution was divided into two equal parts. One part of each solutions was cast onto Teflon petri dishes to achieve their free standing SC prepared SPE films by slow evaporation of the

solvent at room temperature. The second part of each sample was sonicated by ultrasonicator (250 W power, 25 kHz frequency) for 10 min duration with ON-OFF step of 15 s. During ultrasonic processing the stainless steel sonotrode was directly immersed into the electrolyte solution for strong dose of the ultrasound. These ultrasonicated PMMA-LiClO₄-10 wt % PEG and PMMA-LiClO₄-10 wt % PEG-5 wt % MMT solutions were cast onto Teflon petri dishes to achieve their US-SC prepared SPE films. Before the measurements, each electrolyte film was dried in vacuum oven at 40°C for 24 h to remove the residual solvent traces, if any.

Characterizations

The X-ray diffraction (XRD) patterns of the SPE films and their constituents were measured in reflection mode using a PANalytical X'pert Pro MPD diffractometer of Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$) operated at 45 kV and 40 mA. For the XRD measurements, powder samples of LiClO₄ and MMT were tightly filled in the sample holder, whereas pure PMMA and the electrolyte films were placed on the top of the sample holder. The XRD measurements of the samples were carried out in the 2θ range from 3.8° to 30° with a scanning step size of 0.05°/s, at room temperature.

The dielectric dispersion spectra of the SPE films were carried out using an Agilent technologies 4284A precision LCR meter along with Agilent 16451B solid dielectric test fixture. The measurements were performed with 1 V electric signal of linear frequency f range from 20 Hz to 1 MHz over the temperature from 29°C to 55°C. Frequency dependent values of capacitance C_p , parallel resistance R_p and loss tangent $\tan\delta = \epsilon''/\epsilon'$ (dissipation factor D) of the dielectric cell loaded with the SPE film were measured in parallel mode operation. Prior to the sample measurements, the open circuit calibration of the cell was also performed to eliminate the effect of stray capacitance. The frequency dependent values of complex dielectric function $\epsilon^*(\omega) = \epsilon' - j\epsilon''$, real part of ac electrical conductivity $\sigma' = \omega\epsilon_0\epsilon''$, electric modulus $M^*(\omega) = M' + jM''$ and complex impedance $Z^*(\omega) = Z' - jZ''$ of the SPE films were determined by substituting the measured values of C_p , R_p and $\tan\delta$ in the expressions described in detail elsewhere.^{18,40}

RESULTS AND DISCUSSION

Structural Analysis

The XRD patterns of pristine PMMA film, LiClO₄ and MMT powder and SPE films are shown in Figure 1. The observed broad and defused peak of pure PMMA confirms its predominantly amorphous phase.^{18,19} The sharp crystalline peaks of LiClO₄ are found at 21.02° and 23.04°, which confirms its high crystallinity. These LiClO₄ peaks positions are in agreement with the earlier reported results.^{18,19} The crystal reflection peak of MMT found at $2\theta = 7.03^\circ$ is corresponding to its 001 reflection plane of basal spacing $d_{001} = 1.257 \text{ nm}$, whereas the another peak observed at $2\theta = 19.79^\circ$ is due to its 101 crystallographic plane.^{41,42} The XRD patterns of the SPE films have no peaks corresponding to the crystalline peaks of LiClO₄ which reveals that the total amount of salt exists in dissociated form in these films. The dissociation of salt occurs mainly due to formation of ion-dipolar interactions ($\text{C}=\text{O}\cdots\text{Li}^+$) between the carbonyl groups $\text{C}=\text{O}$ of PMMA and

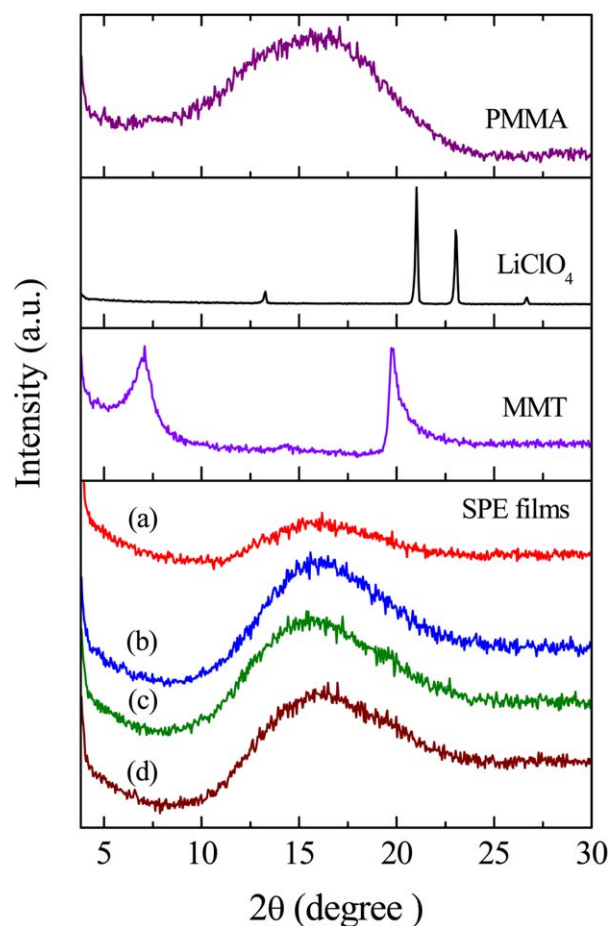


Figure 1. XRD patterns of PMMA film, powder samples of LiClO₄ and MMT, and SPE films of PMMA-LiClO₄-10 wt % PEG prepared by (a) SC method and (b) US-SC method; and PMMA-LiClO₄-10 wt % PEG-5 wt % MMT prepared by (c) SC method and (d) US-SC method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the cations Li⁺ of LiClO₄. In addition to these interactions, the PEG also forms the ion-dipolar ($\text{O}\cdots\text{Li}^+$) interactions in these plasticized SPE films which results in total dissociation of added salt. Further, the disappearance of 001 reflection peak of MMT in the XRD patterns of these SPE film confirms the formation of exfoliated MMT nanosheets. The interactions of $\text{C}=\text{O}\cdots\text{Li}^+$ and $\text{O}\cdots\text{Li}^+$ complexes with the surface charge of MMT nanosheets result in complete exfoliation of the weakly stacked nanosheets in the investigated SPE films. In general, the SPE films having intercalated MMT structures show the 001 reflection peak around 5° in their XRD spectra.³⁵

Dielectric Behavior

Complex permittivity (real part ϵ' and dielectric loss ϵ'') spectra of the SPE films of PMMA-LiClO₄-10 wt % PEG and PMMA-LiClO₄-10 wt % PEG-5 wt % MMT prepared by SC and US-SC methods are shown in Figure 2(a-d). The ϵ' value of a dielectric material is an indicative of energy storing capability, whereas the ϵ'' represents the absorbed electromagnetic energy by the material that's converts into thermal energy by Joule heating effect. The ϵ' spectra of the SPE films have non-

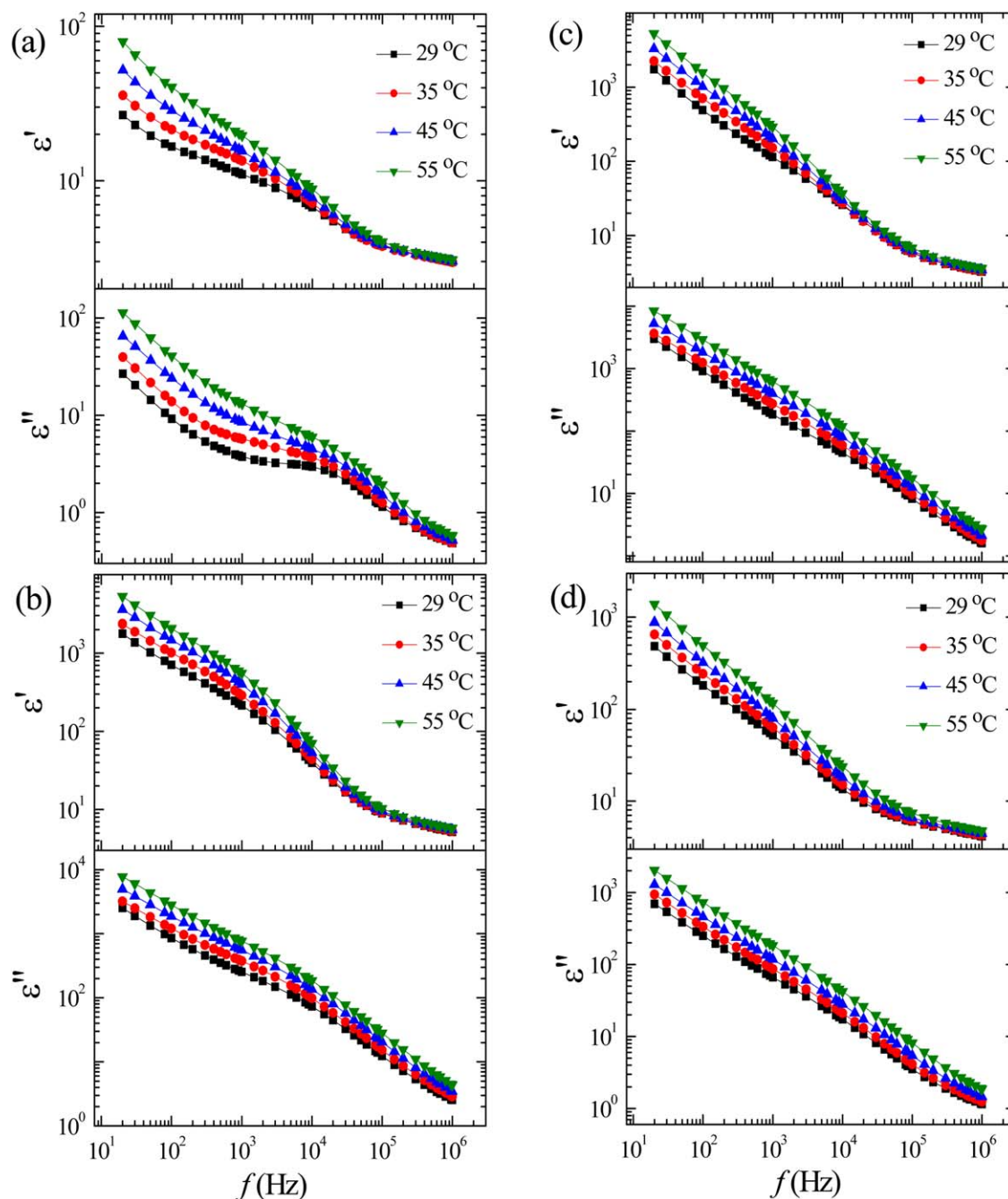


Figure 2. Frequency dependent real part ϵ' and loss ϵ'' of complex dielectric function of the SPE films of PMMA–LiClO₄–10 wt % PEG prepared by (a) SC method and (b) US–SC method, and PMMA–LiClO₄–10 wt % PEG–5 wt % MMT prepared by (c) SC method and (d) US–SC method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

linear decrease with the increase of frequency from 20 Hz, and finally approach the steady state near 1 MHz. Therefore, the ϵ' values at 1 MHz are assigned to the high frequency limiting permittivity ϵ_{∞} which attributes mainly from fast polarization of atoms and electrons under the influence of a time dependent applied electric field.¹⁴ The ϵ_{∞} values of the SPE films are given in Table I which show an increase with the increase of temperature. The frequency dependent ϵ' and ϵ'' values of these SPE films increase with the increase of temperature which is common characteristic of the thermally activated solid polymeric

electrolytes.^{3,5,17,38} Such temperature dependent increase in ϵ' values of these electrolytes is due to the enhancement in dipolar ordering under the influence of applied electric field. In general, the increase of temperature reduces the strength of ion–dipolar complexes which results in the increase of activated dipolar ordering in the SPE materials. This leads to the increases of the total polarization strength and hence there is enhancement of ϵ' and ϵ'' values with rise of temperature. A large increase in ϵ' and ϵ'' values with decrease of frequencies below 1 kHz is due to a dominant contribution of electrode polarization (EP) effect

Table I. Temperature T Dependent Values of High Frequency Limiting Permittivity ϵ_{∞} , Polymer Segmental Motion Relaxation Time τ_s , Conductivity Relaxation Time τ_{σ} , dc Ionic Conductivity σ_{dc} , and Fractional Exponent n of the SPE Films Prepared by Different Methods

T ($^{\circ}\text{C}$)	ϵ_{∞}	τ_s (μs)	τ_{σ} (μs)	$\sigma_{dc} \times 10^7$ (S/cm)	n
PMMA–LiClO ₄ –10 wt % PEG film prepared by SC method					
29	2.96	9.10	3.61	0.16	0.72
35	2.97	9.44	3.08	0.23	0.72
45	3.01	9.38	2.38	0.34	0.72
55	3.09	9.70	1.49	0.53	0.73
PMMA–LiClO ₄ –10 wt % PEG film prepared by US–SC method					
29	5.18	7.77	0.25	4.62	0.64
35	5.31	7.29	0.21	6.18	0.66
45	5.52	5.74	0.15	8.45	0.61
55	5.78	4.32	0.10	12.10	0.62
PMMA–LiClO ₄ –10 wt % PEG–5 wt % MMT film prepared by SC method					
29	3.27	6.48	0.31	3.17	0.63
35	3.32	8.56	0.26	3.89	0.63
45	3.43	8.51	0.17	4.94	0.62
55	3.61	7.41	0.12	7.32	0.63
PMMA–LiClO ₄ –10 wt % PEG–5 wt % MMT film prepared by US–SC method					
29	4.15	32.67	1.86	1.10	0.77
35	4.24	30.86	1.59	1.34	0.78
45	4.44	30.04	0.96	1.92	0.78
55	4.74	19.88	0.57	3.32	0.79

over the bulk dielectric polarization.^{5,6,28,29,43} Mostly, SPE films under the influence of slow reversal electric field of low frequencies form the capacitive electric double layers (EDLs) due to accumulation of ions at the electrode–electrolyte interface. This is termed as EP effect which enhances the net polarization by a large magnitude between the electrodes, and results in a huge increase of ϵ' and ϵ'' values at low frequencies.

From the comparative study of Figure 2(a) with 2(b), and also Figure 2(c) with 2(d), it is observed that the ultrasonic assisted processing of the electrolyte solutions significantly influences the ϵ' and ϵ'' values of these US–SC prepared SPE films as compared with their SC prepared SPE films. Further, the comparisons of Figures 2(a) with 2(c) and also 2(b) with 2(d) reveal that the addition of MMT increases the ϵ' and ϵ'' values when the SPE film is prepared by SC method, whereas these values show a decrease when the same composition SPE film is prepared by US–SC method. These comparative changes in values of ϵ' and ϵ'' spectra of same composition electrolyte sample prepared by different methods infer that the ultrasonication changes orientational state of the exfoliated MMT nanosheets and also their interaction strength with $\text{C}=\text{O}\cdots\text{Li}^+$ and $\text{O}\cdots\text{Li}^+$ complexes. Further, the ϵ'' spectra of SC prepared SPE films have points of inflexion around 10 kHz which are correspond-

ing to polymer chain dielectric relaxation process. But the clear peaks were not observed in the ϵ'' spectra, and therefore the $\tan\delta$ plots were considered in the preceding section in order to determine the value of this relaxation process.

Figure 3(a–d) shows the spectra of real part σ' of complex ac conductivity and the loss tangent $\tan\delta$ of the PMMA–LiClO₄–10 wt % PEG and PMMA–LiClO₄–10 wt % PEG–5 wt % MMT electrolyte films prepared by the SC and US–SC methods. The characteristics of these σ' spectra are EP affected low frequency region, dc plateau, and dc to ac transport in high frequency region. It is found that the high frequency σ' values of these electrolytes obey the Jonscher's power law $\sigma'(\omega) = \sigma_{dc} + A\omega^n$, where σ_{dc} is dc ionic conductivity, A is the pre-exponential factor, and n is the fractional exponent ranging between 0 and 1.⁴⁴ The solid lines in the σ' spectra denote the power law fit to the experimental values at high frequencies, which are obtained by Origin[®] non-linear curve fitting software. The σ_{dc} and n values of these electrolytes, as obtained from Jonscher's power law fit, are given in Table I. Increase in deviation of σ' values from the σ_{dc} values with decrease of frequency in the low frequency region of these SPE films is attributed to initially some contribution of EP effect, but it dominances over bulk properties at lower frequencies.^{3,5,6,38,40} Further, the σ' values of these SPE materials increase with increase of temperature which confirms their thermal activated charge transportation behavior.

The $\tan\delta$ spectra of the investigated SPE films [Figure 3(a–d)] have the relaxation peaks corresponding to dynamics of PMMA chain segments, which are not found in the ϵ'' spectra due to their suppression by significant contribution of EP effect. Further, the unsymmetrical shape of these $\tan\delta$ spectra suggests the uneven distribution of relaxation time in these materials. The variation in shape of $\tan\delta$ spectra of the same composition samples prepared by different methods (SC and US–SC) attributes to variation in ordering of their complexes as also revealed from the different shape of the ϵ' and ϵ'' spectra [Figure 2(a–d)]. It is also observed that the $\tan\delta$ peak intensity value increases with the increase of temperature and its position also changes on the frequency scale. Further, it is found that the $\tan\delta$ peak value of a sample, at fixed temperature, varies with the sample preparation methods, and the trend of variation also alters with the sample composition. The relaxation time values of polymer chain segmental dynamics τ_s for these SPE films are determined by the relation $\tau_s = 1/2\pi f_p(\tan\delta)$, where $f_p(\tan\delta)$ is the value of frequency corresponding to $\tan\delta$ peak. The observed τ_s values of these electrolytes are found of the order of microseconds, and these are recorded in Table I. The τ_s values change anomalously with increase of temperature which suggest that it is highly complex relaxation process. The single relaxation peak in $\tan\delta$ spectra over the six decades of frequency variation confirms the cooperative motion of PMMA segments (α -relaxation) and their bulky ester groups (β -relaxation) in the ion–dipolar complexes of these electrolytes, that is, the τ_s values of these electrolytes may be assigned to the merged $\alpha\beta$ -relaxation process.

Figure 4(a–d) shows the electric modulus (real part M' and imaginary part M'') spectra of the PMMA–LiClO₄–10 wt %

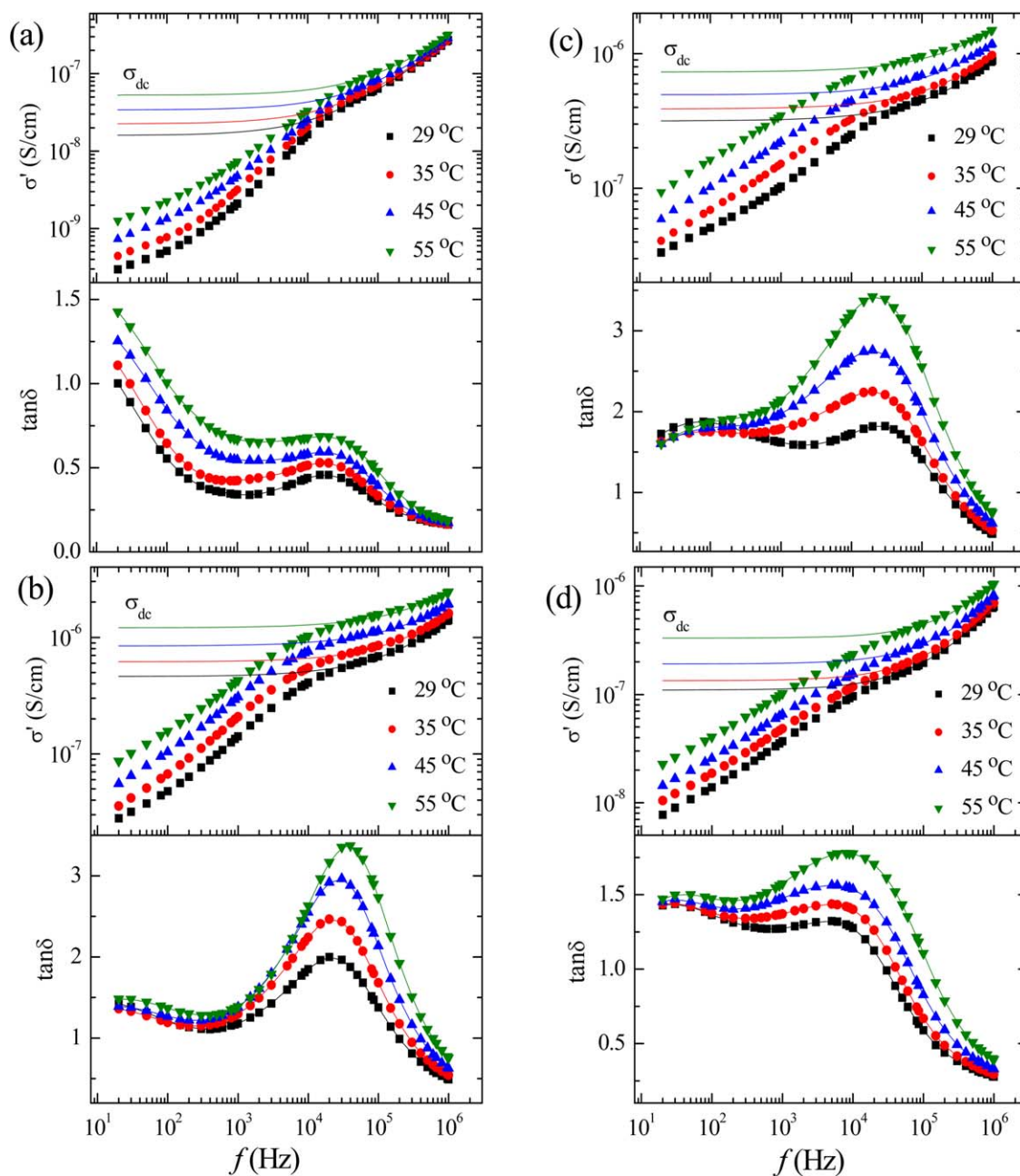


Figure 3. Frequency dependent real part of ac conductivity σ' and loss tangent $\tan\delta$ of SPE films of PMMA–LiClO₄–10 wt % PEG prepared by (a) SC method and (b) US–SC method; and PMMA–LiClO₄–10 wt % PEG–5 wt % MMT prepared by (c) SC method and (d) US–SC method. The solid lines in σ' spectra are the Jonscher's power law fit to the experimental values at high frequencies. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PEG and PMMA–LiClO₄–10 wt % PEG–5 wt % MMT electrolyte films prepared by SC and US–SC methods. Due to unity value of $M^*(\omega)$ and $\epsilon^*(\omega)$ product, that is, $M^*(\omega) \cdot \epsilon^*(\omega) = 1$; the EP effect, electrode–electrolyte contact effect, influence of electrode material and impurities absorbed in the electrolyte do not mask the features of bulk materials in their M' and M'' spectra.^{3–6,38,39,43,45} It is found that the M' and M'' values of the studied SPE films in the low frequency region are close to zero (Figure 4) which confirms the suppression of EP effect in the modulus formalism. The dispersion of

M' and M'' values in high frequency is attributed to ionic conduction relaxation in the electrolytes (dc to ac transport).^{3,5,8,36–38,43} The M'' spectra of the SPE films exhibit a single relaxation peak. In such type of M'' spectra, the frequency region to the left side of the relaxation peak frequency is where the cations are mobile over long distances, and the region to the right is where the ions are spatially confined to their potential wells.⁵ Further, ions have long-range to short-range mobility in these electrolytes when the frequency value exceeds the M'' peak frequency value.

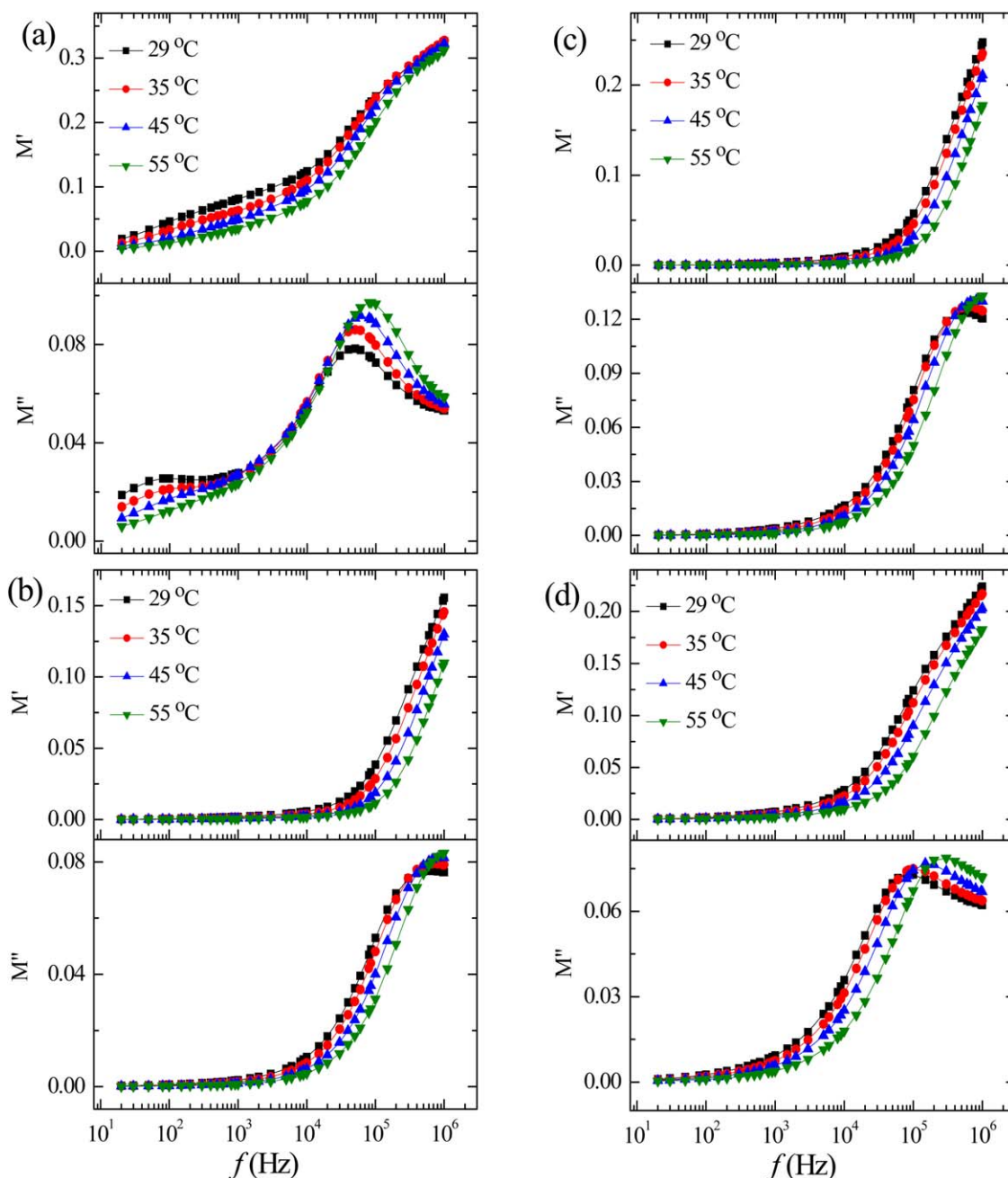


Figure 4. Frequency dependent real part M' and loss M'' of complex electric modulus of SPE films of PMMA–LiClO₄–10 wt % PEG prepared by (a) SC method and (b) US–SC method; and PMMA–LiClO₄–10 wt % PEG–5 wt % MMT prepared by (c) SC method and (d) US–SC method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The comparative shape of M'' spectra and the frequency position of the relaxation peaks also reveal that the structural behavior of these electrolytes is influenced by the sample preparation methods and the addition of MMT nanofiller. It is observed that the relaxation peaks of M'' spectra at different temperatures have gradual shift towards the high frequency side with increase of temperature. This shift is due to enhancement of free volume in the material, which also facilitates the mobility of ionic charge. This behavior reveals that the ionic relaxation is thermally activated, and transportation of charge carrier takes place

by hopping mechanism in these SPE materials. The M'' peak frequency $f_{p(M)}$ values of these electrolytes are used to determine the modulus relaxation time τ_M values by the relation $\tau_M = 1/2\pi f_{p(M)}$. The τ_M is also referred to the ionic conduction relaxation time τ_σ because of its direct correlation with the ions transportation in SPE materials. The evaluated τ_σ , that is, τ_M values of these electrolytes at different temperatures are recorded in Table I. These τ_σ values are found about one order of magnitude higher than the corresponding τ_s values for these SPE films.

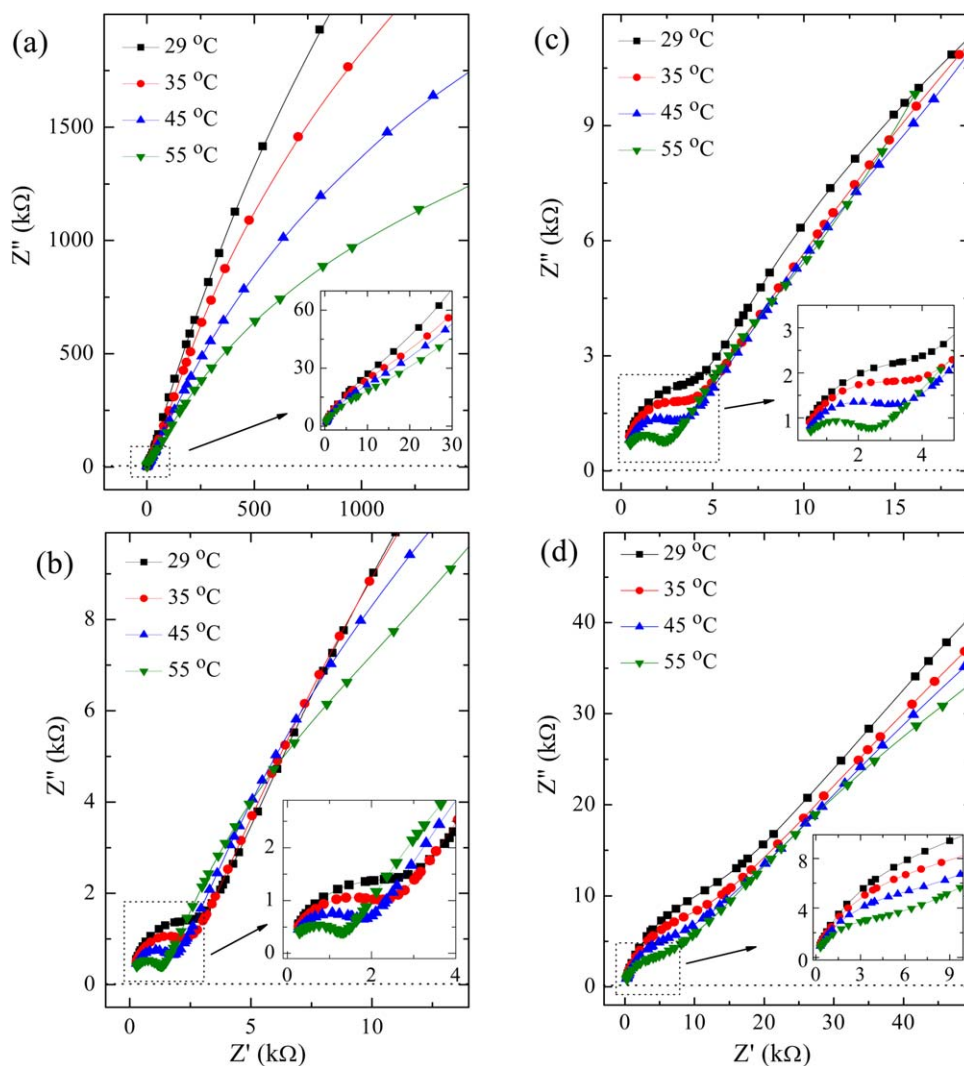


Figure 5. Complex impedance plane plots (Z'' vs. Z') of SPE films of PMMA–LiClO₄–10 wt % PEG prepared by (a) SC method and (b) US–SC method; and PMMA–LiClO₄–10 wt % PEG–5 wt % MMT prepared by (c) SC method and (d) US–SC method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To have better insight into the electrical properties of the materials, the complex impedance plane plots (Z'' vs. Z') of PMMA–LiClO₄–10 wt % PEG and PMMA–LiClO₄–10 wt % PEG–5 wt % MMT electrolyte films prepared by SC and US–SC methods are depicted in Figure 5(a–d). The frequency values of experimental data points increase on going from right to left on these plots. These plots have arcs shapes in the high frequency region corresponding to the bulk properties of electrolyte materials (enlarged views of the arcs are shown in the insets of Figure 5). The appearance of spikes having the slope less than 90° at lower frequencies in the impedance plots represents the EDL capacitive effect, which occurs owing to polarization at the electrode/electrolyte interface. Such behavior of the shape of complex impedance plane plots is very common for the SPE materials.^{2,3,8,14,17,45} The bulk properties of such SPE film can be described by a parallel combination of resistance R_b and geometrical capacitance C_g with a constant phase element (CPE) in series.¹⁷ In the electrochemical impedance analysis technique,

the σ_{dc} values of the electrolytes are determined using the R_b values estimated from the shape of Z'' versus Z' plots.^{2,14,17} The R_b values of the electrolytes are assumed equal to Z' values where the arc and spike intersection occurs on the real impedance axis.

Many times, the arcs of SPE films corresponding to bulk properties are not found perfectly distinguishable from their spikes. Such behavior of impedance plots can be seen for PMMA–LiClO₄–10 wt % PEG film prepared by SC method and PMMA–LiClO₄–10 wt % PEG–5 wt % MMT film prepared by US–SC method [Figure 5(a,d)]. For these SPE films, the estimation of R_b value from their impedance plots may be incorrect. Therefore, the σ_{dc} values in the present study are determined by the Jonscher's power law fit to their σ' spectra. The n values obtained from Jonscher's power law are also related to the nature of ion transport mechanism in the SPE materials. The n values of the studied electrolytes are found less than unity [in the range 0.6–0.8 (Table I)], which confirms that in these

materials the ions transportation occurs through hopping mechanism. Such behavior of ion transportation in solid polymeric electrolytes has also been reported in the earlier studies.^{3,5,8,18,38,43} In this mechanism, ions motion involves activated hopping over energy barriers that separates adjacent conducting sites.⁴⁶ Further, for the occurrence of an ion hopping from one coordination site to another in the polymer matrix, the initially occupied site relaxes and the new site deforms to hold the incoming ion. In this process, ionic motion is expected to be coupled to local dynamical modes of the polymer chain. For the studied electrolytes, the n values are found significantly low as compared with unity confirming the forward hop relaxation of the ions¹⁷ which is needed to enhance the ionic conductivity of the SPE materials.

Correlation Between Ionic Conductivity and Relaxation Time

The σ_{dc} value of a solid electrolyte material is given by the relation $\sigma_{dc} = \sum n_i \mu_i q_i$, where n_i , μ_i , and q_i are the charge carriers density, mobility of free charge carriers (unpaired ions) and the charge of the i th ion (monovalent, divalent, etc.), respectively. In these studied SPE films, the ions are monovalent (Li^+ and ClO_4^-). The XRD patterns of these electrolytes (Figure 1) have revealed that the total salt is in dissociated form. Therefore, the ions concentration for these electrolytes may be assumed fixed. Further, in the SPE films, the bulky anions have comparatively poor mobility and mostly remain unassociated with the host polymer.^{5,6,18,38} Considering these facts, it is clear that the ionic conductivity of the investigated SPE films is mainly governed by their cations mobility. The mobility values of the cations depend on the polymer chain dynamics and the favorable ion conductive paths in the ion-dipolar complexed structures of the electrolytes.^{3,5-8,10,38}

Initially, we compare the conductivity values of PMMA-LiClO₄-10 wt % PEG electrolyte films prepared by SC and US-SC methods. It is found that the σ_{dc} value of the US-SC prepared electrolyte film is 29 times higher as compared with that of the SC prepared electrolyte film, at ambient temperature (Table I). At 55°C, the comparative increase of σ_{dc} value is about 23 times for the US-SC prepared electrolyte film. The large increase of σ_{dc} value of this electrolyte film prepared by US-SC method is favored by the increase of its polymer segmental dynamics (low τ_s value), and also by comparatively low value of conductivity relaxation time τ_σ (Table I). It seems that due to ultrasonic assisted processing of electrolyte solution, its SPE film has relatively faster transient-type dynamical complexes i.e. the barrier hindrance is relatively low during the transportation of cations. The decrease of potential barrier favors the number of successful forward ion hops leading to increase of ionic conductivity of such SPE film.

Now, we consider the effect of MMT nanofiller on the σ_{dc} value of the electrolyte film when it is prepared by SC method. Table I shows that the σ_{dc} value of SC prepared electrolyte film increases by 20 times on the addition of 5 wt % MMT, at room temperature. The XRD spectra of this SC prepared PMMA-LiClO₄-10 wt % PEG-5 wt % MMT film reveals that the MMT structures are completely exfoliated. But, there may be some parallel-type arrangement of the exfoliated nanosheets which form favorable ion conductive paths due to which the ionic conductivity

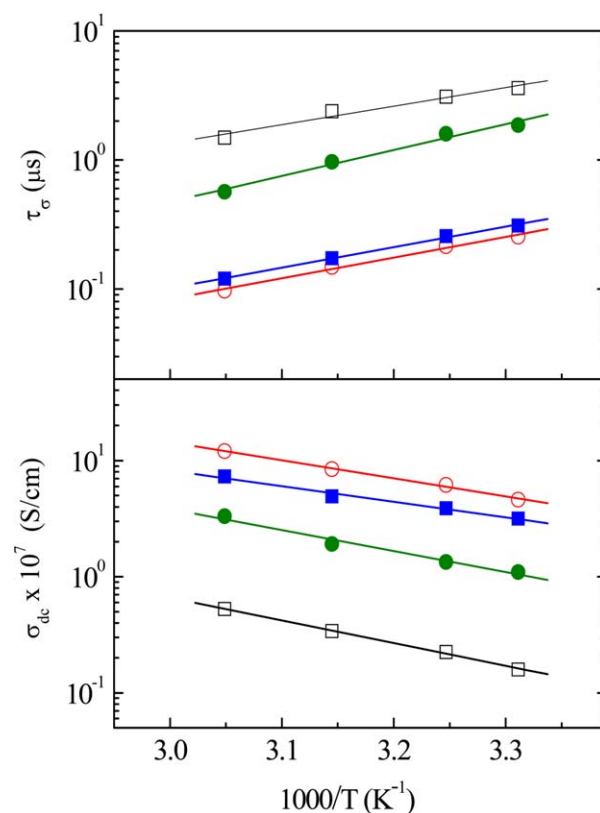


Figure 6. Reciprocal temperature dependence of conductivity relaxation time τ_σ and dc ionic conductivity σ_{dc} of SPE films of PMMA-LiClO₄-10 wt % PEG prepared by (□) SC method and (○) US-SC method; and PMMA-LiClO₄-10 wt % PEG-5 wt % MMT prepared by (■) SC method and (●) US-SC method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increases. Besides this fact, the decrease of τ_σ value with addition of MMT in the electrolyte film also favors the increase of its σ_{dc} value. Table I shows that a decrease in σ_{dc} value is observed for PMMA-LiClO₄-10 wt % PEG-5 wt % MMT film when prepared by US-SC method in comparison to its preparation by SC method. This decrease in conductivity value confirms that under the influence of ultrasonication, some random reorientation of the exfoliated MMT nanosheets has occurred. Such randomly oriented nanosheets hinder the motion of cations coupled polymer chain as revealed from the increase of its τ_s and τ_σ values. Beside these results, the σ_{dc} value of the US-SC prepared and MMT added electrolyte film is found about six times higher as compared with the MMT free electrolyte film prepared by SC method (Table I). Further, the room temperature ionic conductivity values of these plasticized electrolytes are found about one order of magnitude higher than that of without plasticized PMMA-LiClO₄ electrolytes.^{19,27} The σ_{dc} values of these investigated electrolytes are also found close to that of the organomodified MMT nanofiller added electrolytes.²⁰ Further, as compared with these PEG plasticized PMMA-LiClO₄-MMT electrolytes, the σ_{dc} values of PMMA-LiClO₄ plasticized by ethylene carbonate and propylene carbonate with MMT nanofiller are found higher by one to two orders of magnitude. In these systems, significant increase in σ_{dc} values was observed owing to the addition of large

Table II. Values of Conductivity Activation Energy E_σ and Relaxation Activation Energy E_τ of SPE Films Prepared by Different Methods

Methods of film preparation	E_σ (eV)	E_τ (eV)
PMMA–LiClO ₄ –10 wt % PEG film		
SC method	0.39	0.29
US–SC method	0.31	0.32
PMMA–LiClO ₄ –10 wt % PEG–5 wt % MMT film		
SC method	0.27	0.32
US–SC method	0.36	0.40

amount of these plasticizer in electrolytes which turned the materials into gel-type electrolytes.^{21,26,27,47}

The σ_{dc} values of these plasticized SPE films enhance with the increase of their temperature, whereas the relaxation time τ_σ decreases (Table I). Reciprocal temperature dependence behavior of τ_σ and σ_{dc} values for PMMA–LiClO₄–10 wt % PEG and PMMA–LiClO₄–10 wt % PEG–5 wt % MMT films are shown in Figure 6. It can be seen that on logarithmic scale the τ_σ and σ_{dc} values exhibit an activated behavior obeying the Arrhenius relations $\tau = \tau_0 \exp(E_\tau/k_B T)$ and $\sigma_{dc} = \sigma_0 \exp(-E_\sigma/k_B T)$, respectively. Conductivity activation energy E_σ values for the electrolyte films are determined from the slope of Figure 6, and these values are recorded in Table II. It is found that the E_σ value is a little low for the US–SC prepared PMMA–LiClO₄–10 wt % PEG film as compared with that of the SC prepared electrolyte film of same composition. But reverse trend in variation of these E_σ values is observed with the same preparation methods for the MMT nanofiller added electrolyte films. The E_σ values of these electrolytes are found in the range from 0.27 to 0.39 eV, which are in agreement with the activation energies of several other investigated SPEs.^{3,17,38,48} The low E_σ values indicate that the mobile ions face lower energy barrier during hopping process. Further, these low E_σ values also support the transient-type dynamical behavior of the ion-dipolar complexes of these electrolytes. A small variation in E_σ values of the electrolytes with addition of MMT nanofiller, and the change of sample preparation methods reveals that the concentration of mobile ions are same in these different films, and the relative changes observed in their σ_{dc} values are due to variation in the cations mobility only. The conductivity relaxation activation energy E_τ values of these electrolytes are also determined from the least square straight-line fit of their Arrhenius plots. The evaluated E_τ values of the electrolytes are given in Table II. These E_τ values of the SPE films are found nearly equal to that of their E_σ values (Table II). This result infers that the transportation of ions in the plasticized and MMT added these PMMA–LiClO₄-based SPE films occurs by hopping mechanism. In this mechanism, the Li⁺ ions overcome the same barrier while relaxing as well as while conducting. This type of ions transportation mechanism is also found in the PEO–LiClO₄-based SPE films.^{5,38}

CONCLUSIONS

The dielectric dispersion and structural dynamics of the PMMA–LiClO₄–10 wt % PEG and PMMA–LiClO₄–10 wt %

PEG–5 wt % MMT electrolyte films prepared by SC and US–SC methods were reported, at different temperatures. The effects of sample preparation methods and the MMT nanofiller on the dynamical structures, dielectric properties, ionic conductivity, and the ion conduction mechanism in these SPE films were explored. It is observed that the dielectric properties of PMMA–LiClO₄–10 wt % PEG film increase when it is prepared by US–SC method, whereas for the PMMA–LiClO₄–10 wt % PEG–5 wt % MMT electrolyte film these properties have decrease. All the samples have peak in their $\tan\delta$ spectra corresponding to merged $\alpha\beta$ -relaxation of PMMA, and its dynamical behavior is governed by the strength of ion-dipolar interactions in the complexes. In case of PMMA–LiClO₄–10 wt % PEG electrolyte, the ultrasonic assisted processing results in increase of ambient temperature σ_{dc} value by 29 times as compared with that of the SC prepared film of same composition. The σ_{dc} value of the plasticized electrolyte film also enhances on the addition of 5 wt % MMT nanofiller. For these electrolyte materials, it is revealed that the ion conduction is through hopping mechanism, which is governed by the conductivity relaxation time in the transient-type dynamical ion-dipolar complexes. The temperature dependent σ_{dc} and τ_σ values of the investigated SPE films obey the Arrhenius behavior. The values of conductivity and relaxation activation energies of these SPE materials are found low (≤ 0.4 eV) and nearly same despite the change of film preparation methods and also with the addition of MMT nanofiller. The significant ionic conductivity value of these electrolytes at ambient temperature confirms their suitability in preparation of ion conducting electrochromic devices.

ACKNOWLEDGMENTS

One of the authors SC is thankful to the DST, New Delhi for the award of SERB Fast Track Young Scientist research project no. SR/FTP/PS-013/2012. Author RJS is grateful to the Department of Science and Technology (DST), New Delhi for providing financial assistance through research project no. SR/S2/CMP-0072/2010.

REFERENCES

- Scrosati, B.; Garche, J. *J. Power Sources* **2010**, *195*, 2419.
- Syzdek, J.; Armand, M.; Marcinek, M.; Zalewska, A.; Żukowska, G.; Wieczorek, W. *Electrochim. Acta* **2010**, *55*, 1314.
- Mohapatra, S. R.; Thakur, A. K.; Choudhary, R. N. P. *J. Power Sources* **2009**, *191*, 601.
- Money, B. K.; Hariharan, K.; Swenson, J. *Solid State Ionics* **2012**, *225*, 346.
- Karmakar, A.; Ghosh, A. *Curr. Appl. Phys.* **2012**, *12*, 539.
- Choudhary, S.; Sengwa, R. J. *Mater. Chem. Phys.* **2013**, *142*, 172.
- Wang, Y.; Li, B.; Ji, J.; Zhong, W. H. *J. Power Sources* **2014**, *247*, 452.
- Choudhary, S.; Sengwa, R. J. *Ionics* **2011**, *17*, 811.
- Fahmi, E. M.; Ahmad, A.; Rahman, M. Y. A.; Hamzah, H. J. *Solid State Electrochem.* **2012**, *16*, 2487.

10. Karan, N. K.; Pradhan, D. K.; Thomas, R.; Natesan, B.; Katiyar, R. S. *Solid State Ionics* **2008**, *179*, 689.
11. Lim, C. S.; Teoh, K. H.; Liew, C. W.; Ramesh, S. *Mater. Phys. Chem.* **2014**, *143*, 661.
12. Ramesh, S.; Liew, C. W.; Ramesh, K. *J. Appl. Polym. Sci.* **2013**, *127*, 2380.
13. Uma, T.; Mahalingam, T.; Stimming, U. *Mater. Chem. Phys.* **2005**, *90*, 245.
14. Das, S.; Ghosh, A. *AIP Adv.* **2015**, *5*, 027125.
15. An, Y.; Cheng, X.; Zuo, P.; Liao, L.; Yin, G. *Mater. Chem. Phys.* **2011**, *128*, 250.
16. Agrawal, R. C.; Sahu, D. K.; Mahipal, Y. K.; Ashrafi, R. *Mater. Chem. Phys.* **2013**, *139*, 410.
17. Nath, A. K.; Kumar, A. *Electrochim. Acta* **2014**, *129*, 177.
18. Sengwa, R. J.; Choudhary, S. *J. Phys. Chem. Solids* **2014**, *75*, 765.
19. Shukla, N.; Thakur, A. K. *Ionics* **2009**, *15*, 357.
20. Shukla, N.; Thakur, A. K. *Solid State Ionics* **2010**, *181*, 921.
21. Deka, M.; Kumar, A. *Electrochim. Acta* **2010**, *55*, 1836.
22. Kumar, D.; Hashmi, S. A. *J. Power Sources* **2010**, *195*, 5101.
23. Ramesh, S.; Wong, K. C. *Ionics* **2009**, *15*, 249.
24. Ramesh, S.; Shanti, R.; Durairaj, R. *J. Non-Cryst. Solids* **2011**, *357*, 1357.
25. Ahmad, S.; Saxena, T. K.; Ahmad, S.; Agnihotry, S. A. *J. Power Sources* **2006**, *159*, 205.
26. Meneghetti, P.; Qutubuddin, S.; Webber, A. *Electrochim. Acta* **2004**, *49*, 4923.
27. Chen, H. W.; Lin, T. P.; Chang, F. C. *Polymer* **2002**, *43*, 5281.
28. Choudhary, S.; Sengwa, R. J. *Ionics* **2012**, *18*, 379.
29. Choudhary, S.; Bald, A.; Sengwa, R. J. *Indian J. Pure Appl. Phys.* **2013**, *51*, 769.
30. Xu, Y.; Brittain, W. J.; Xue, C.; Eby, R. K. *Polymer* **2004**, *45*, 3735.
31. Tiwari, R. R.; Natarajan, U. *J. Appl. Polym. Sci.* **2007**, *105*, 2433.
32. Clarke, N.; Hutchings, L. R.; Robinson, I.; Elder, J. A.; Collins, S. A. *J. Appl. Polym. Sci.* **2009**, *113*, 1307.
33. Dhibar, A. K.; Mallick, S.; Rath, T.; Khatua, B. B. *J. Appl. Polym. Sci.* **2009**, *113*, 3012.
34. Di Pasquale, G.; Pollicino, A. *J. Appl. Polym. Sci.* **2015**, *132*, 41393.
35. Choudhary, S.; Sengwa, R. J. *J. Appl. Polym. Sci.* **2015**, *132*, 41311.
36. Sengwa, R. J.; Dhatarwal, P.; Choudhary, S. *Electrochim. Acta* **2014**, *142*, 359.
37. Sharma, P.; Kanchan, D. K. *Ionics* **2013**, *19*, 1285.
38. Sengwa, R. J.; Choudhary, S. *Indian J. Phys.* **2014**, *88*, 461.
39. Sengwa, R. J.; Kaur, K.; Choudhary, R. *Polym. Int.* **2000**, *49*, 599.
40. Sengwa, R. J.; Sankhla, S.; Choudhary, S. *Ionics* **2010**, *16*, 697.
41. Choudhary, S.; Sengwa, R. J. *J. Appl. Polym. Sci.* **2014**, *131*, 39898.
42. Sengwa, R. J.; Choudhary, S. *J. Appl. Polym. Sci.* **2014**, *131*, 40617.
43. Pradhan, D. K.; Choudhary, R. N. P.; Samantary, B. K. *Mater. Chem. Phys.* **2009**, *115*, 557.
44. Jonscher, A. K. *Dielectric Relaxation in Solids*; Chelsea Dielectric Press: London, **1983**.
45. Sengwa, R. J.; Dhatarwal, P.; Choudhary, S. *Curr. Appl. Phys.* **2015**, *15*, 135.
46. Rolling, B.; Martiny, C.; Funke, K. *J. Non-Cryst. Solids* **1999**, *249*, 201.
47. Deka, M.; Kumar, A. *J. Solid State Electrochem.* **2010**, *14*, 1649.
48. Ghelichi, M.; Qazvini, N. T.; Jafari, S. H.; Khonakdar, H. A.; Farajollahi, Y.; Scheffler, C. *J. Appl. Polym. Sci.* **2013**, *129*, 1868.