

Preparation and characterization of biodegradable poly (ϵ -caprolactone)-based gel polymer electrolyte films

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Abstract: Biodegradable polymer electrolyte films based on poly(ϵ -caprolactone) (PCL) in conjunction with lithium tetrafluoroborate (LiBF_4) salt and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF_4) ionic liquid were prepared by solution cast technique. The structural, morphological, thermal, and electrical properties of these films were examined using X-ray diffraction (XRD), optical microscopy (OM), differential scanning calorimetry (DSC), and impedance spectroscopy. The XRD and OM results reveal that the pure PCL possesses a semi-crystalline nature and its degree of crystallinity decreases with the addition of LiBF_4 salt and EMIMBF_4 ionic liquid. DSC analysis indicates that the melting temperature and enthalpy are apparently lower for the 40 wt% EMIMBF_4 gel polymer electrolyte as compared with the others. The ambient temperature electrical conductivity increases with increasing EMIMBF_4 concentration and reaches a high value of $\sim 2.83 \times 10^{-4} \text{ S cm}^{-1}$ for the 85 PCL:15 $\text{LiBF}_4 + 40 \text{ wt% EMIMBF}_4$ gel polymer electrolyte. The dielectric constant and ionic conductivity follow the same trend with increasing EMIMBF_4 concentration. The dominant conducting species in the 40 wt% EMIMBF_4 gel polymer electrolyte determined by Wagner's

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polarization technique are ions. The ionic conductivity of this polymer electrolyte ($\sim 2.83 \times 10^{-4} \text{ S cm}^{-1}$) should be high enough for practical applications.

Keywords: Biodegradable polymer electrolytes; electrical conductivity; Dielectric constant; transference numbers.

1. Introduction

Researchers all over the world are currently focusing on developing the ion-conducting gel polymer electrolytes due to their potential ionic device applications in lithium ion batteries, fuel cells, supercapacitors, solar cells, electrochemical display devices [1-4]. The gel polymer electrolytes offer numerous advantages, such as improved safety, light weight, low cost, leakage proof and good thermal stability in conjunction with ease fabrication into desired shapes and sizes. In addition, they exhibit high electrical conductivity, high energy density and wide electrochemical stability window, which makes them suitable candidates/electrolytes for technological applications. The gel polymer electrolyte (GPEs) is a hybrid electrolyte and it offers a combined beneficial characteristic of both liquid electrolyte and solid electrolyte systems. Such a gel polymer electrolyte is usually prepared by mixing a polymer host, inorganic salt and liquid solvent/plasticizers. The most commonly used plasticizers are aprotic organic solvents such as ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC) and dimethyl carbonate (DMC) [5, 6]. These organic liquids are usually high volatile, corrosive, flammable. Due to these properties, the use of organic solvents/plasticizers suffers thermal stability and electrical/electrochemical properties of gel polymer electrolytes. Moreover, these organic solvents are also responsible for the narrower electrochemical window and working

voltage range of devices based on gel polymer electrolytes. Recently, to conquer these problems, new classes of material, i.e., ionic liquids (e.g., 1-butyl-4-methylpyridinium bis(trifluoromethanesulfony) imide (BMpyTFSI), poly 1-ethyl 3-(2-methacryloyloxy ethyl) imidazolium iodide (PEMEImI), and 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄)) are used as the solvent or plasticizer to develop high ionic conductivity gel polymer electrolytes for solid state ionic device applications. The ionic liquids are basically room temperature molten salt typically consisting of bulky asymmetric organic cations and inorganic anions, which possess the specific properties such as wide liquid-phase, non-volatility, non-flammability, negligible vapor pressure at room temperature, wide electrochemical stability window, excellent thermal and chemical stability, high ionic conductivity, and ability to dissolve a variety of compounds [7, 8]. The method of incorporating ionic liquids into the polymer matrix is also easy and is realized by a simple solution casting method. The ionic liquid incorporated gel polymer electrolytes are a new class of material called the ionic liquid gel polymer electrolytes (ILGPEs). Therefore, it is the area of our current interest to develop ionic liquid incorporated gel polymer electrolytes and study their structural, thermal and electrical properties for ionic device applications.

Global warming is a serious worrying environmental issue currently in the world. Hence the use of biodegradable materials as conducting gel polymer electrolytes can mitigate the environmental problems due to its eco-friendliness and short biodegradable time. Several biodegradable polymers such as cellulose, starch, chitosan, poly (vinyl alcohol) and poly (ϵ -caprolactone) are being used as the host polymer for the preparation of gel polymer electrolytes [9-12]. Among these polymers, polyester-based biodegradable polymer is one of the most promising polymer ionic conductors because its unique structures are able to facilitate ion

transport. Poly (ϵ -caprolactone) (PCL) is a polyester-based biodegradable polymer and is nontoxic and widely used in different applications [13, 14]. It is derived from crude oil and prepared by ring opening polymerization of ϵ -caprolactone using a stannous octoate as catalyst. Due to its low glass transition temperature, the polymer chain exhibits segmental motion which helps transport of ions from one complexation site to another [15, 16]. The PCL also possesses a carbonyl group and a Lewis base ester oxygen which can coordinate lithium ions. A strong electron donating nature of this ester oxygen of carbonyl would tend to complex with lithium ion, and thus the PCL can be selected as a good polymer host for preparation of gel polymer electrolytes [12, 17]. Lithium tetrafluoroborate (LiBF_4) salt possesses many advantages such as low cost, good environmental impacts, low lattice energy, low moisture and high solubility. It can be easily dissolved, producing ions for ionic conduction in the polymer matrix. The EMIMBF₄ ionic liquid is a green solvent and contains bulky asymmetric organic cations (EMIM^+) and inorganic anions (BF_4^-). This ionic liquid possesses various specific properties such as non-volatility, non-flammability, eco-friendliness, excellent thermal and chemical stability, and ability to dissolve a variety of polymers. Further, the LiBF_4 salt and EMIMBF₄ ionic liquid contain the common anion (BF_4^-). All these properties play an important role in modifying the structural, surface morphological, thermal and electrical properties of polymer electrolytes. Due to the above causes, the LiBF_4 salt and EMIMBF₄ ionic liquid have been chosen here for the development of environment-friendly PCL-based ILGPEs.

In this work, PCL: LiBF_4 complexed polymer electrolytes with various LiBF_4 concentrations were prepared and the optimal composition were determined. It led to the development of environmental friendly biodegradable gel polymer electrolytes based on

85PCL:15LiBF₄+ x EMIMBF₄ system. The effect of different EMIMBF₄ concentrations and on their structural, morphological, thermal and electrical properties were studied. **2. Experimental**

2.1. Materials

The poly (ϵ -caprolactone) (PCL) with Mn=80 kDa was procured from Sigma Aldrich and used as received. Lithium tetrafluoroborate (LiBF₄) salt and 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) ionic liquid were obtained from Sigma Aldrich and dried in an oven at 40 °C for 24 h and stored in a vacuum desiccator prior to use. Tetrahydrofuran (THF) with purity 99% from Sigma Aldrich was used as the common solvent for the polymer film preparation. Fig. 1 shows the chemical structure of poly (ϵ -caprolactone), Lithium tetrafluoroborate and 1-Ethyl-3-methylimidazolium tetrafluoroborate.

2.2. Polymer electrolyte film preparation

Pure PCL and PCL:LiBF₄ complexed polymer electrolyte films with different LiBF₄ salt concentrations (5, 10, 15, and 20 wt%) were prepared using a standard solution casting technique. The predetermined quantities of PCL and LiBF₄ salts were added to THF and magnetically stirred at ambient temperature for 12 h to get a homogeneous mixture. The stirred solutions were cast onto glass petri dishes allowed to evaporate slowly at ambient temperature, followed by vacuum drying to obtain free standing polymer electrolyte films at the bottom of dishes. 85PCL:15LiBF₄ is identified as an optimum composition by XRD analysis.

A series of EMIMBF₄ ionic liquid incorporated gel polymer electrolyte films containing the 85PCL:15LiBF₄+x EMIMBF₄ (where x = 0, 10, 20, 30 and 40 wt%) were prepared by solution cast technique. The optimized quantities of PCL polymer and LiBF₄ salt were dissolved in a common solvent tetrahydrofuran (THF) by continuous magnetic stirring at 40 °C for 5 h to obtain a homogeneous mixture. Then different quantities of EMIMBF₄ ionic liquid were added

to the 85PCL:15PCL homogenous mixture and the stirring was continued for 12 h to obtain a homogeneous viscous solution. Finally, the obtained solutions were poured into glass petri dishes and allowed to evaporate the common solvent at ambient temperature to obtain free-standing ILGPE films. Up to the concentration of 40 wt% EMIMBF₄ ionic liquid, the ILGPEs were stable, and beyond this concentration the physical nature of the film was found to be not stable enough for further investigations. The prepared films were stored in a vacuum desiccator to avoid any environmental moisture absorption prior to subsequent characterization. The thickness of these films was determined using screw gage and it was approximately 150 μm .

2.3. Characterization

XRD is the most useful method for the determination of crystal structure, crystallite size and crystallinity of the materials. XRD patterns of the LiBF₄ salt and polymer films were recorded using a computer-controlled D/max Rigaku X-ray diffractometer with Cu K α radiation [wavelength (λ) = 0.1541 nm] as the source at 40 kV with a scanning range of 5 to 65°. Surface morphology and microscopic feature of the polymer films were examined using Optical Microscopy (OM). In order to understand the thermal history and stability of present polymer films, Differential Scanning Calorimetry (DSC) measurements were made on an STA 449F3 jupiter thermal analyzer at a heating rate of 5 °C min⁻¹ under a nitrogen atmosphere in the temperature range of 30 to 150 °C. The impedance spectroscopy is a powerful technique for the investigation into the electrical properties of polymer electrolyte films. The electrical measurements of the polymer films were conducted using an impedance analyzer (PSM 1735, Newton 4th Ltd, UK) over the frequency range 1 Hz – 1 MHz. In the measurements, the ILGPE films were sandwiched between a pair of stainless steel foil. The prepared samples were cut into circular pieces and dried at 35 °C in vacuum condition for 1 h before the electrical measurements

for reducing the environmental moisture effects. The nature of the conducting species (ionic or electronic) in the polymer electrolyte is characterized by the transport number, which is defined as the fraction of current carried by ions (anions and cations) (t_{ion}) or electrons (t_{ele}) in the material in terms of total conductivity (σ). The transference number of 40 wt% EMIMBF₄ gel polymer electrolyte was determined by Wagner's polarization technique [18, 19]. In this technique a constant potential 1.5 V was applied to a symmetric cell in the configuration SS/polymer electrolyte/SS. The resulting static current was monitored as a function of time using a Keithley (model 2400) programmable electrometer in which stainless steel acted as blocking electrode.

3. Results and discussion

3.1. Structural analysis

XRD data were used to determine the crystal structure and nature of biodegradable polymer films. The XRD patterns of Pure PCL, LiBF₄ salt, PCL:LiBF₄ complexed polymer electrolytes and 85PCL:15LiBF₄+ *x* EMIMBF₄ gel polymer electrolytes with different EMIMBF₄ concentrations are shown in Figs. 2 (a) and 2 (b). The XRD profile of LiBF₄ salt shows intensive sharp peaks which indicate its crystalline nature. The observed sharp peaks at $2\theta=21.90^\circ$, 23.963° , 25.99° , 26.428° , 27.847° , 37.42° , 38.498° are well matched with the standard data from JCPDS card numbers: 0-1431 and 40-0664. The XRD pattern of pure PCL exhibits three significant sharp crystalline peaks at $2\theta=21.4^\circ$, 22° , and 23.7° which are assigned to the (110), (111) and (200) orientation planes, respectively. These sharp peaks are attributed to the crystalline phase of PCL, which originates from the ordering of polymer side chains due to the intermolecular interaction between PCL chains through the hydrogen bonding. In addition to these crystalline peaks, the broad hump between 15° and 25° is also observed and it is attributed

to the amorphous phase of PCL. These observations confirm that the pure PCL polymer possesses a semi-crystalline nature and its crystal structure is orthorhombic. The sharp peaks for the LiBF_4 salt are found to be absent in the complexed system, indicating the complete dissociation of salt in the polymer matrix. Furthermore, it is also observed from Fig. 2 (a) that the intensity of all crystalline peaks for 80PCL:20 LiBF_4 complexed polymer electrolyte is higher than those for 85PCL:15 LiBF_4 polymer electrolyte, indicating the higher degree of crystallinity in the 20 wt% LiBF_4 complexed polymer electrolyte system. It is in a good agreement with the fact that the 85PCL:15 LiBF_4 complexed polymer electrolyte has high amorphous nature and that the 15 wt% LiBF_4 is the optimum concentration.

A comparison of all the spectra reveals that when the LiBF_4 salt and EMIMBF₄ ionic liquid are incorporated into the PCL matrix, the intensities of all the crystalline peaks decrease (see in Fig. 2 (a) and Fig. 2 (b)), suggesting an increase in the amorphicity of the PCL matrix. This may be due to the disruption of the semi-crystalline structure of the polymer by salt and ionic liquid dissolution. It is also observed that all the crystalline peaks are broadened and their relative intensities decrease with increasing LiBF_4 salt and EMIMBF₄ ionic liquid concentration from 5 to 15 wt% and 10 to 40 wt% respectively, which is ascribed to the increase in the amorphous nature of the host polymer. When the LiBF_4 salt and EMIMBF₄ ionic liquid are added to the PCL host, the interaction between PCL- LiBF_4 and PCL-EMIMBF₄ leads to a decrease in the intermolecular interaction among the polymer chains, thereby reducing the crystalline phase and hence increasing the amorphous region. Furthermore, the peaks are slightly shifted, the peak at $2\theta = 22.0^\circ$ is disappeared, and the peak intensity at 26.68° increases with increasing EMIMBF₄ ionic liquid concentration, indicating the formation of the new complex system.

The degree of crystallinity of the polymer films are calculated from the de-convoluted (see in Fig. 2 b) XRD peaks using the following equation [20]

$$X_c = \frac{A_c}{A_c + A_a} \times 100 \quad (1)$$

where A_c is the total area under the crystalline peaks and A_a is the area under the amorphous peak. The calculated degree of crystallinity of the pure PCL is 43.52% which decreases gradually with an increase of LiBF_4 salt concentration and then reaches a minimum value 29.26% at 15 wt% LiBF_4 concentration. This degree of crystallinity value is further decreased with increasing EMIMBF₄ ionic liquid concentration and reaches a much lower value of approximately 21.13% for the 40 wt% EMIMBF₄ ionic liquid gel polymer film. The 40 wt% EMIMBF₄ ionic liquid incorporated gel polymer electrolyte film exhibits a high amorphicity. The polymeric chain in amorphous phase is more flexible, which results in an enhancement of segmental motion in the polymer, thereby increasing the electrical conductivity. Hence the gel polymer electrolyte film containing 40 wt% EMIMBF₄ ionic liquid shows a high electrical conductivity.

3.2. Surface morphology analysis

In this study, optical microscopy was used to observe the surface morphology of the PCL polymer film and its changes with the addition of LiBF_4 salt and EMIMBF₄ ionic liquid. Fig. 3 shows the optical micrographs of the pure PCL and 85PCL:15LiBF₄+ x EMIMBF₄ ionic liquid gel polymer electrolyte films ($x = 0, 20$ and 40 wt%).

The micrograph of the pure PCL film shows a spherulitic texture with dark boundary regions, demonstrating its semi-crystalline nature. This type of surface morphology was also

observed for other semi-crystalline polymers, such as (PEO)₆:NaPO₃ and PEO: Mg(CF₃SO₃)₂ polymer electrolytes [21, 22]. The spherulitic texture in the polymer film exhibits its lamellar crystalline nature and the dark boundaries indicate the amorphous content in the polymer as can be seen in Fig. 3a. The lamellar was developed through regular polymer chain folding, leading to a long range order. The lamella radiate out from a central nucleating point. The amorphous phase occupies the regions between the lamella so that the spherulites are embedded in the amorphous matrix. These inter and intra spherulitic amorphous regions may or may not be of the same composition and exhibit distinct physical properties [23]. With the addition of LiBF₄ salt and EMIMBF₄ ionic liquid in the PCL polymer matrix, there are significant changes in surface morphology (see Figs. 3b and c), i.e., the dark boundary regions increase, indicating an increase in amorphous phase in the PCL matrix. This could be due to the structural disruption of the PCL polymer by the LiBF₄ salt and EMIMBF₄ ionic liquid dissolution. When the LiBF₄ salt and EMIMBF₄ ionic liquid are added to the PCL polymer, they introduce ions (Li⁺, EMIM⁺ and BF₄⁻) to the polymer matrix, which may interact with the host polymer and creates a structural disruption, thereby enhancing the amorphous nature. Furthermore, it is also observed that with increasing EMIMBF₄ ionic liquid concentration from 20 to 40 wt% the dark boundary regions are further increased and there is no longer spherulitic texture (see Fig. 3d), meaning that there is a large percentage of amorphous phase in the 40 wt% EMIMBF₄ ionic liquid gel polymer electrolyte film. Clearly, these morphological changes are in good agreement with the XRD results.

3.3. Thermal analysis

DSC measurements were carried out to determine the melting temperature (T_m) and degree of crystallinity of polymer electrolyte films. Fig. 4 shows the DSC thermograms of pure

PCL, 85PCL:15LiBF₄ and 85PCL:15LiBF₄+40 wt% EMIMBF₄ gel polymer electrolytes in the temperature range of 30 to 90 °C. Obviously the pure PCL shows a relatively sharp endothermic peak at 64 °C, indicating the melting temperature of pure PCL. This is attributed to the crystalline melting of PCL, which shows the presence of uncomplexed crystalline phase. With the addition of 15 wt% LiBF₄ salt and 40 wt% EMIMBF₄ ionic liquid in the PCL matrix, the melting temperature of pure PCL shifts to lower temperatures. The decrease in melting temperature upon the additives is not uncommon, which is associated with the decrease in the size of spherulites and their surface free energy [24, 25]. As a result of additional amorphous surroundings being trapped in or adjacent to the crystalline matrix, the suppressed crystalline part of the PCL complex would melt at a lower temperature [26]. Moreover, it is also observed that there are no extra peaks present with the addition of LiBF₄ salt and EMIMBF₄ ionic liquid, indicating that there is no chemical reaction occurring between the host polymer and additives.

The DSC melting peak area gives the crystalline melting enthalpy (ΔH_m) of the polymer electrolyte. It is the energy in the form of heat absorbed per unit weight of the polymeric sample. In general, the melting enthalpy (ΔH_m) is proportional to the degree of crystallinity of the polymer electrolyte [27, 28]. It is observed from Fig. 4 that the intensity of melting endothermic event decreases and broadens with the addition of LiBF₄ and EMIMBF₄. The observed changes suggest the decrease in the degree of crystallinity or the increase in the amorphicity of the host PCL polymer. Since the more additives are accommodated in the host PCL, they suppress the crystalline phase in the polymer. The polymeric chain in the amorphous phase is more flexible and mobile, which results in an enhancement of segmental motion of the polymer [29]. The 85PCL:15LiBF₄+40 wt% EMIMBF₄ gel polymer electrolyte exhibits a small ΔH_m (33.85 J g⁻¹), demonstrating its high amorphous nature. Undoubtedly, these results are consistent with those

obtained in XRD and OM. From the XRD, OM and DSC. It can be claimed that the 85PCL:15LiBF₄+40 wt% EMIMBF₄ gel polymer electrolyte exhibits a high amorphous nature. The electrical conductivity is usually supported by the amorphous phase of a polymer film and thus this electrolyte film may be expected to show a high electrical conductivity because of its high amorphicity. The detailed electrical conductivity studies of the prepared polymer electrolytes are discussed in the next section.

3.4. Electrical conductivity analysis

Fig. 5 shows the room temperature Nyquist impedance plots of the 85PCL:15LiBF₄+ *x* EMIMBF₄ gel polymer electrolyte films with various EMIMBF₄ ionic liquid concentrations. Obviously, each plot contains a semicircular arc and an inclined spike, which is a typical characteristic behavior of ionic conducting solids with blocking electrodes [30]. The high frequency semicircle is associated with the parallel combination of bulk resistance due to the migration of ions and with bulk capacitance due to the immobile polymer chains. The low frequency spike represents the formation of double layer capacitor at the electrode–electrolyte interface. The magnitude of blocking double-layer capacitance (C_{dl}) may be obtained from any position on the straight line portion using $Z_w=1/(2\pi fC_{dl})$, where Z_w is the impedance corresponding to the position and f is the frequency. The inclination of the spike at an angle less than 90° to the real axis indicates the inhomogeneous nature of the electrode–electrolyte interface. The bulk resistance (R_b) of the ILGPE was obtained by the intercept of semicircle with the real axis. It can be seen in Fig. 5 that the magnitude of bulk resistance decreases with increasing EMIMBF₄ ionic liquid concentration. The electrical conductivity of the gel polymer electrolyte film is calculated by.

$$\sigma = \frac{l}{R_b A} \quad (2)$$

where l is the thickness of the polymer electrolyte film, A is the electrode area and R_b is the bulk resistance.

The variation of room temperature electrical conductivity with EMIMBF₄ concentration is showed in Fig. 6. It can be seen that the electrical conductivity of 85PCL:15LiBF₄+ x EMIMBF₄ polymer electrolyte increases with increasing EMIMBF₄ ionic liquid concentration and then reaches a high value at 40 wt% EMIMBF₄ concentration. At room temperature, the observed electrical conductivity for 85PCL:15LiBF₄ is $7.95 \times 10^{-6} \text{ S cm}^{-1}$ and is $2.83 \times 10^{-4} \text{ S cm}^{-1}$ for 40 wt% EMIMBF₄ gel polymer electrolyte. The 40 wt% EMIMBF₄ electrical conductivity is 100 order higher than that of the 85PCL:15LiBF₄ system, it is comparable with those available in the literature [12, 17]. It is worth mentioning that this electrical conductivity value could be even higher because the effective electrode area could be smaller than the apparent electrode area employed in the calculation since the sample-electrode contact is usually not 100%. The increasing electrical conductivity with EMIMBF₄ concentration may be due to the increase of mobile charge species and the enhancement of polymer chain flexibility. The 85PCL:15LiBF₄+EMIMBF₄ gel polymer electrolyte system has a common anion, and hence it could have fewer chances for the formation of cross-contact ion pairs. This also leads to an increase in electrical conductivity.

In the microscopic picture, the magnitude of the electrical conductivity of the ILGPE depends on charge carrier concentration (n_i), charge of the mobile carrier (q_i) and carrier mobility (μ_i) as described by

$$\sigma = n_i q_i \mu_i \quad (3)$$

According to aforementioned equation, the enhancement of the electrical conductivity can be achieved by increasing n_i as well as μ_i . With the addition of EMIMBF₄ ionic liquid in the polymer, the new charge carriers (EMIM⁺ and BF₄⁻) are introduced and then the overall charge carrier concentration in the ILGPE system is increased, which is responsible for the increase of the electrical conductivity. At a lower EMIMBF₄ concentration, the number of charge carriers is predominantly responsible for the electrical conduction. At a higher EMIMBF₄ concentration, the mobility of ions tends to play a key role in the electrical conduction. The increased electrical conductivity with a high EMIMBF₄ concentration is due to the increase of polymer chain flexibility and thereby the increase of segmental motion, which may provide the ion conduction pathways [31]. More flexibility of the polymer chains also means a greater disorder in its arrangement/structure, which may result in an increased amorphous phase in the ILGPEs. Within the amorphous matrix, the mobile ions may travel a long distance (i.e., the mobility increases) before getting deviated from their paths, thus leading to an increased electrical conductivity.

Study of dielectric constant (ϵ') of the gel polymer electrolyte films may help to understand the enhancement of the electrical conductivity and the polarization effect at the electrode-electrolyte interface. The dielectric constant is a dimensionless entity (or parameter) and it measures the energy stored in the material during each cycle, which is returned to the electric field at the end of the cycle. The dielectric constant also represents the amount of dipole alignment in a given volume. It can be calculated by

$$\epsilon' = \frac{Z''}{\omega C_0 (Z'^2 + Z''^2)} \quad (4)$$

where C_0 is the vacuum capacitance ($C_0 = \epsilon_0 A / l$ in units of F or S Ω^{-1}), ω is the angular frequency ($\omega = 2\pi f$), ϵ_0 is the vacuum permittivity of ($\epsilon_0 = 8.854 \times 10^{-12}$ F m $^{-1}$), A is the electrode-sample contact area, and l is the polymer film thickness.

Fig. 7 shows the frequency dependence of dielectric constant (ϵ') for the 85PCL:15LiBF $_4$ + x EMIMBF $_4$ gel polymer electrolyte films with different EMIMBF $_4$ concentrations. A dispersion with high ϵ' values is observed in the low frequency range, which depicts the blown up region of the dielectric data. In the low frequency range, the ions are capable of moving in the direction of the electric field, but they are unable to be transported to the external circuit because of the blocking electrodes. As a result, the ions are trapped near the electrode-electrolyte interface, leading to the formation of a hetero-charge layer called the electrode polarization [32]. This indicates that the electrode polarization and space charge effects are predominant in the low frequency. With the addition of EMIMBF $_4$ ionic liquid in the 85PCL:15LiBF $_4$ complex, the dielectric constant is amplified, which could be due to the high dielectric constant of EMIMBF $_4$. An additive with a high dielectric constant always have a large dissociation ability to prevent the ion-pair formation or a high effectiveness on shielding the interionic columbic attraction between cations and anions, resulting in a high dielectric constant of the system.

It is seen from Fig. 7 that the dielectric constant decreases continuously with increasing frequency and reaches a stable value at very high frequencies (MHz). It is noticed that a rapid decrease in dielectric constant occurs over a frequency range of 1 Hz–100 Hz and the dielectric constant is almost independent of frequency at high frequencies (MHz). At the very high frequencies, the periodic reversal of the field takes place so quickly that the charge carriers can

hardly have time to orient themselves in the field direction, leading to the observed frequency-independent ϵ' behavior [33].

In order to observe the EMIMBF₄ concentration dependence of ϵ' for the gel polymer electrolyte, a fix frequency value must be chosen randomly. The EMIMBF₄ concentration dependence of ϵ' at randomly selected frequencies (100 Hz, 200 kHz, 500 Hz and 1.07 kHz) is shown in Fig. 8. The selected frequency range of 100 Hz to 2 kHz is the range of electrode polarization where it is easier to see the ϵ' variation with EMIMBF₄ content. In this range, the relative permittivity may be considered as the dielectric constant. As can be seen from Fig. 8, ϵ' increases with increasing EMIMBF₄ concentration and reaches a high value at 40 wt% EMIMBF₄ concentration. This type of behavior is also observed in the electrical conductivity studies (see Fig. 6). The increase of ϵ' is due to the increase of the density of mobile charge carriers. With the addition of EMIMBF₄ ionic liquid in the polymer-salt system, the new ions are introduced and thus the density of charge carriers is increased, leading to an increase in the dielectric constant of the gel polymer electrolyte system.

Recently, Sownthari et al. [12, 28] prepared a new gel polymer electrolyte based on the 75PCL:25ZnTr complexed system doped with different concentrations of EMIMTF₂N ionic liquid by solution cast technique and studied their structural, thermal and electrical properties. The XRD results reveal that the 75PCL:25ZrTf system possesses a semi-crystalline structure and its crystallinity decreases with increasing ionic liquid concentration. The electrical conductivity increases with increasing ionic liquid concentration, reaching a high value of 1.1×10^{-4} S cm⁻¹ at room temperature. Woo et al. [17] prepared proton conducting gel polymer electrolytes based the 74PCL:26NH₄SCN system and doped with different ethylene carbonate (EC) concentrations and examined their structural, thermal and electrical properties. The DSC results indicate that both

the melting temperature (T_m) and relative crystallinity decrease with increasing EC content up to 50 wt% and their values are 44.1 °C and 16.8%, respectively. At room temperature, the electrical conductivity rises with increasing EC concentration, reaching a high value of $1.01 \times 10^{-4} \text{ S cm}^{-1}$ for the 74PCL:26NH₄SCN+50EC system. It is also reported that the variation of ϵ' with EC concentration follows the same trend as the room temperature electrical conductivity. Obviously, the present results are well consistent with theirs and the obtained room-temperature electrical conductivity of $2.83 \times 10^{-4} \text{ S cm}^{-1}$ for the 85PCL:15LiBF₄+40 wt% EMIMBF₄ gel polymer electrolyte is well comparable with the reported values.

The transference number measurement embodies the nature of species responsible for the conductivity in the present polymer electrolyte system, i.e., the quantity of current carried by ions and electrons to the total conductivity. The transport number of any particle (ions or electrons) is defined as the ratio between the conductivity of particle to the total conductivity. The d.c. polarization current versus time plots of 40 wt% EMIMBF₄ gel polymer electrolyte is shown in Fig. 9. In this figure the initial current is contributed by the ions and electrons. The initial current is expressed as the total current (i.e., $I_i = I_T$), which is the sum of the ionic and electronic current ($I_i = I_T = I_{ion} + I_{ele}$). The initial current on application of a potential was proportional to the applied field and then the polarization current starts decreasing with time and finally reaches a constant value after a long time polarization. During the polarization process the ions are blocked at the SS electrode and the final current is only contributed by electronic current ($I_f = I_{ele}$). The transference numbers (t_{ion} , t_{ele}) are calculated by using following equations.

$$t_{ion} = (I_i - I_f) / I_i \quad (5)$$

$$t_{ele} = (I_f / I_i) \quad (6)$$

where I_i and I_f are the initial and final currents recorded from the d.c. polarization current versus times plots.

The ionic transference number (t_{ion}) for 85PCL:15LiBF₄+40 wt% EMIMBF₄ gel polymer electrolyte systems is found to be approximately 0.99. This suggests that the charge transport in this gel polymer electrolyte is predominantly due to ions, which has potential to satisfy the requirement of practical ionic device applications [32]. It should be noted that no electronic transport is expected in gel polymer electrolytes because the liquid electrolytes are entrapped in the inert network of polymer hosts and liquid-like ion transport takes place. The major ionic contribution to the total conductivity could be associated with lithium ions due to their smaller ionic size and higher mobility.

4. Conclusions

Novel biodegradable PCL-based ionic liquid gel polymer electrolyte films are fabricated by solution casting, and their structural, morphological, thermal, and electrical properties are systematically studied. The pure PCL possesses a semi-crystalline structure, which significantly changes with the addition of LiBF₄ salt and EMIMBF₄ ionic liquid. The degree of crystallinity of PCL decreases with the addition of LiBF₄ salt and EMIMBF₄ ionic liquid. A low degree of crystallinity is obtained for the 85 PCL:15 LiBF₄ + 40 EMIMBF₄ system, being ~21.13 %. The electrical conductivity and dielectric constant values increase with increasing EMIMBF₄ concentration due to the increase in the density of mobile charge carriers and the decrease in the crystallinity of the host polymer. The 40 wt% EMIMBF₄-incorporated gel polymer electrolyte exhibits a high electrical conductivity of

$\sim 2.83 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature. The ionic transference number of the electrolyte is ~ 0.99 , indicating that the conductivity is almost 100 % ionic conductivity in nature.

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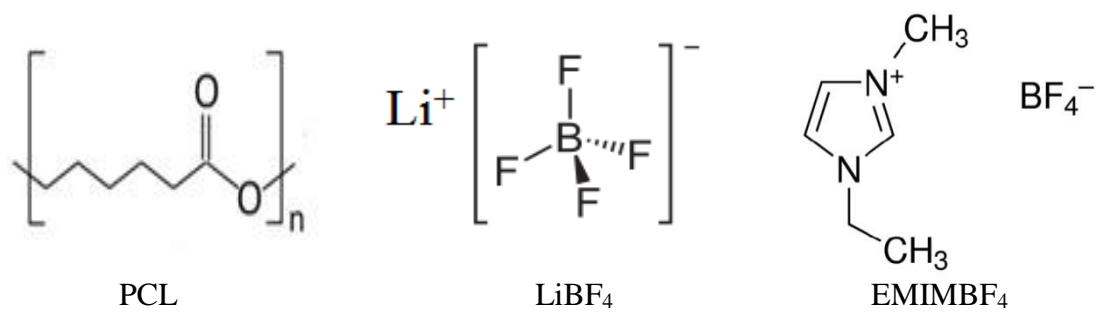
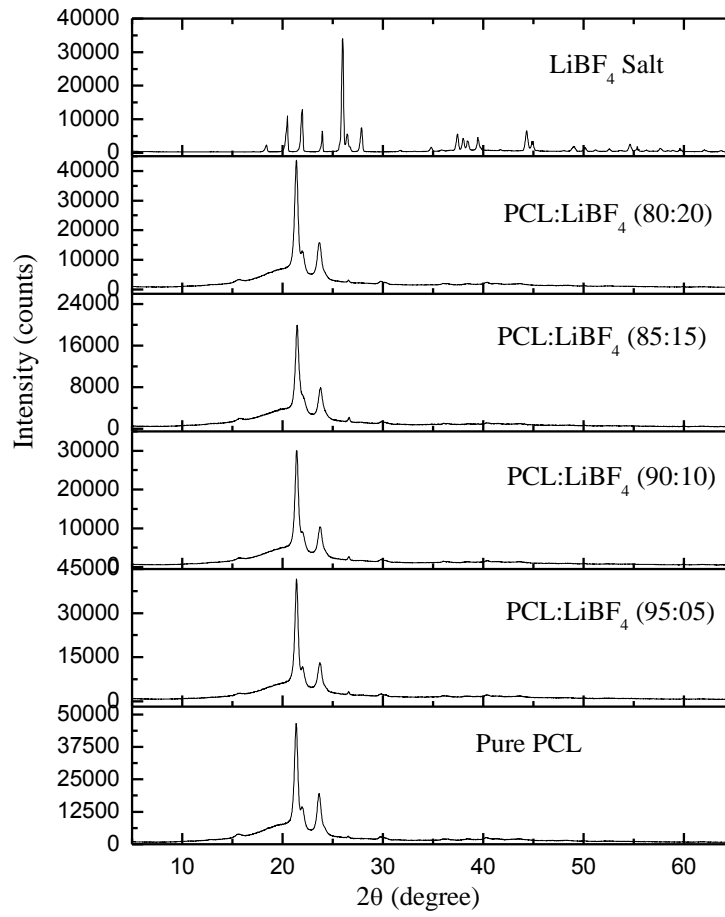


Fig. 1. Molecular structures of PCL, LiBF₄ and EMIMBF₄ [18]



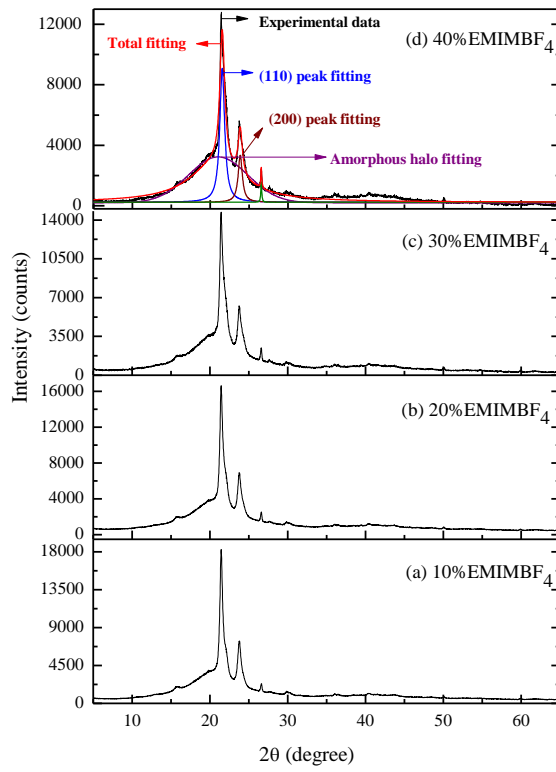


Fig. 2 XRD patterns of **a** pure PCL, LiBF₄ salt and PCL:LiBF₄ complexed polymer electrolytes and **b** 85PCL:15LiBF₄+x EMIMBF₄ gel polymer electrolytes (x=10, 20, 30, and 40 wt%)

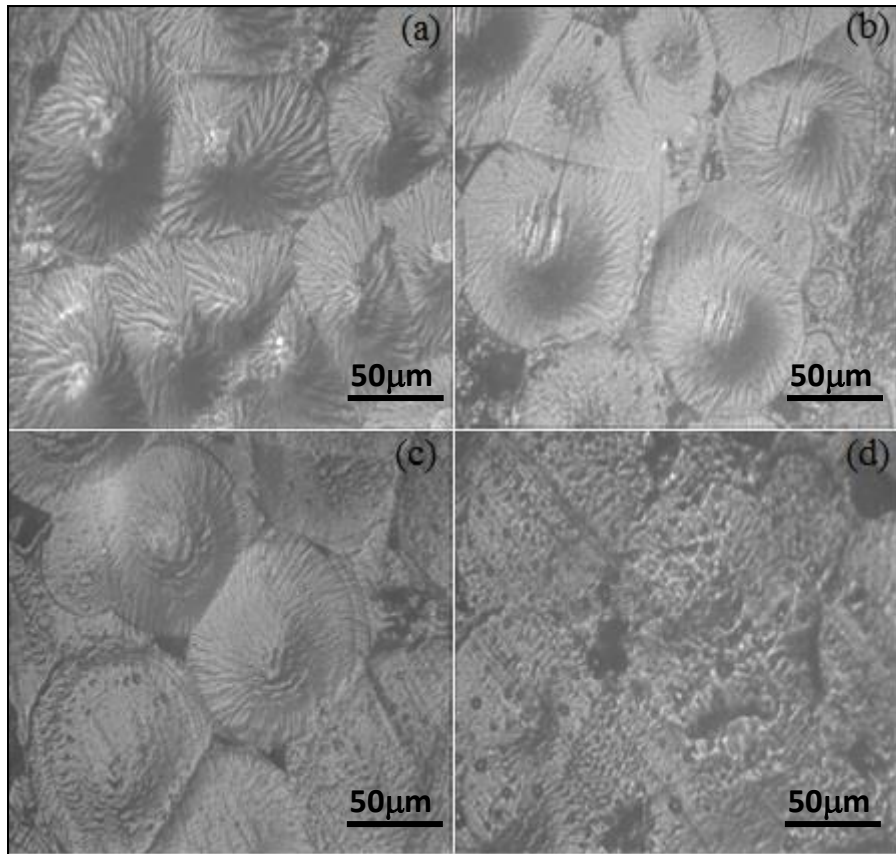


Fig. 3. Optical micrographs of (a) pure PCL, (b) 85PCL:15LiBF₄, (c) 85PCL:15LiBF₄+20EMIMBF₄, and (d) 85PCL:15LiBF₄+40EMIMBF₄

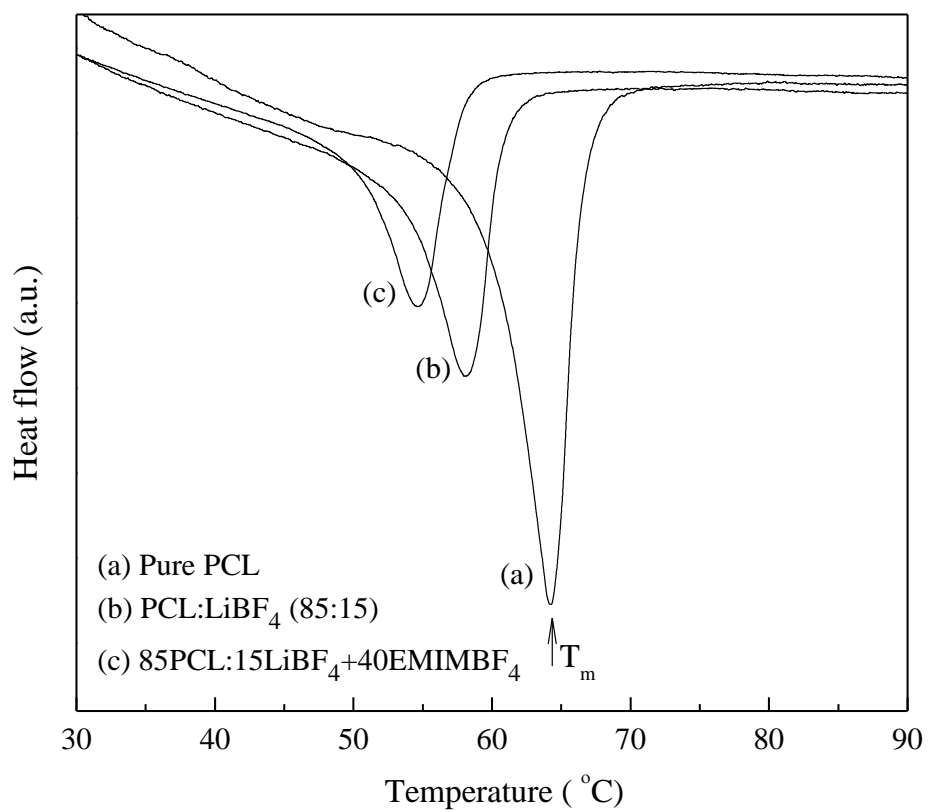


Fig. 4. DSC thermograms of pure PCL, 85PCL:15LiBF₄ and 85PCL:15LiBF₄+40EMIMBF₄

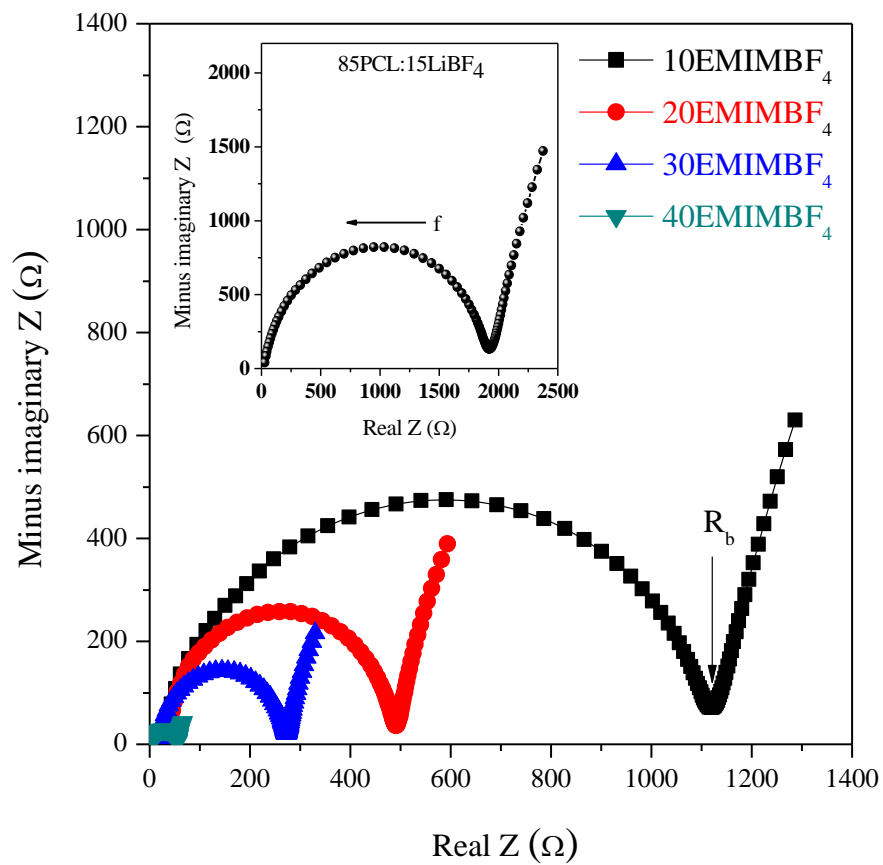


Fig. 5. Nyquist impedance plots of the 85PCL:15LiBF_{4+x} EMIMBF₄ gel polymer electrolyte films ($x=0, 10, 20, 30$ and 40 wt%) at room temperature (f = frequency; R_b = bulk resistance)

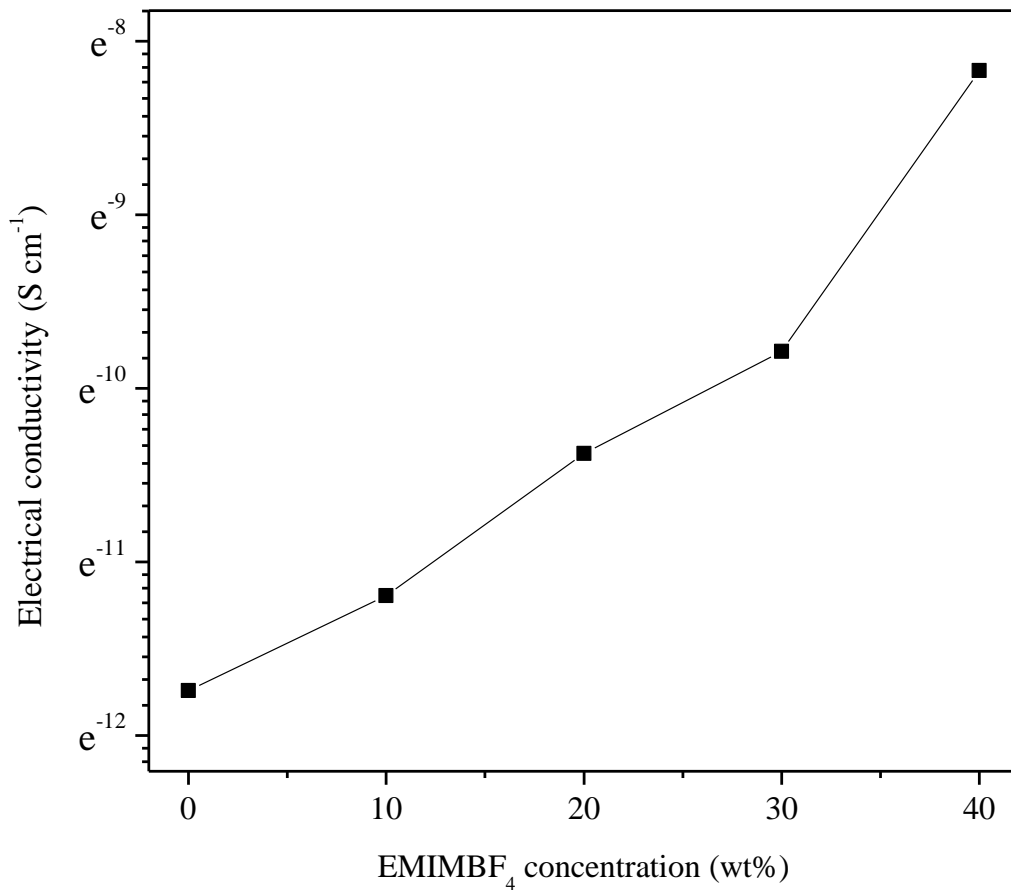


Fig. 6. EMIMBF₄ concentration dependence of electrical conductivity at room temperature for the 85PCL:15LiBF₄+EMIMBF₄ gel polymer electrolyte films

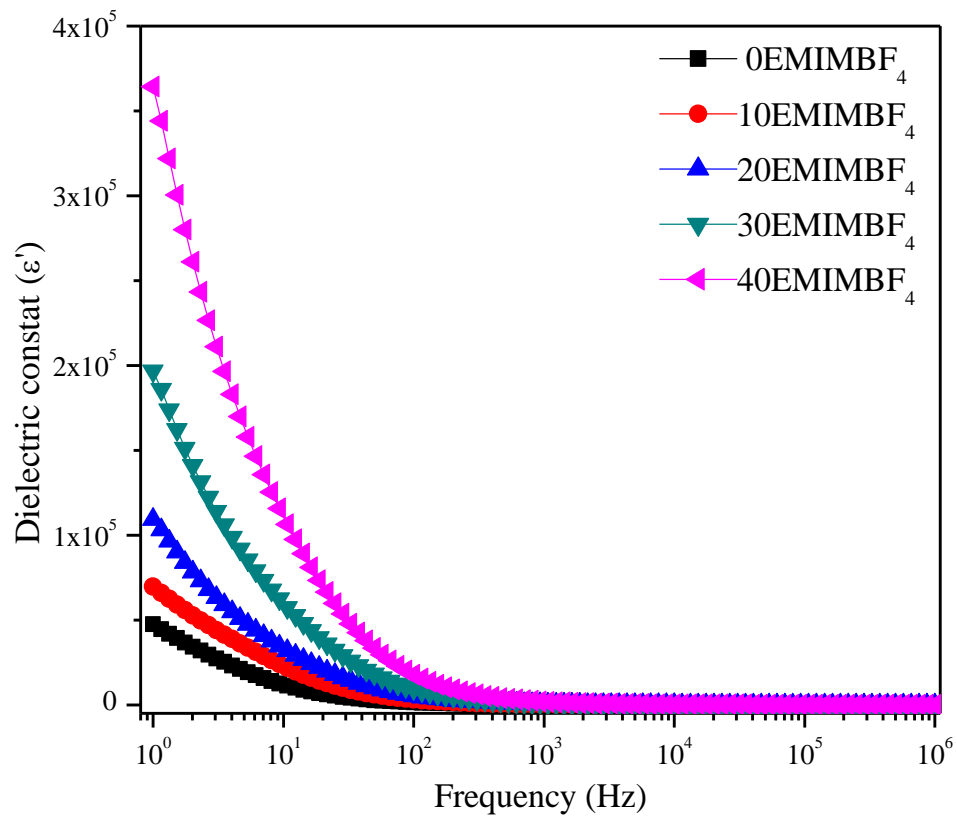


Fig.7. Frequency-dependent dielectric constant of the 85PCL:15LiBF₄+EMIMBF₄ gel polymer electrolyte films with different EMIMBF₄ concentrations at room temperature

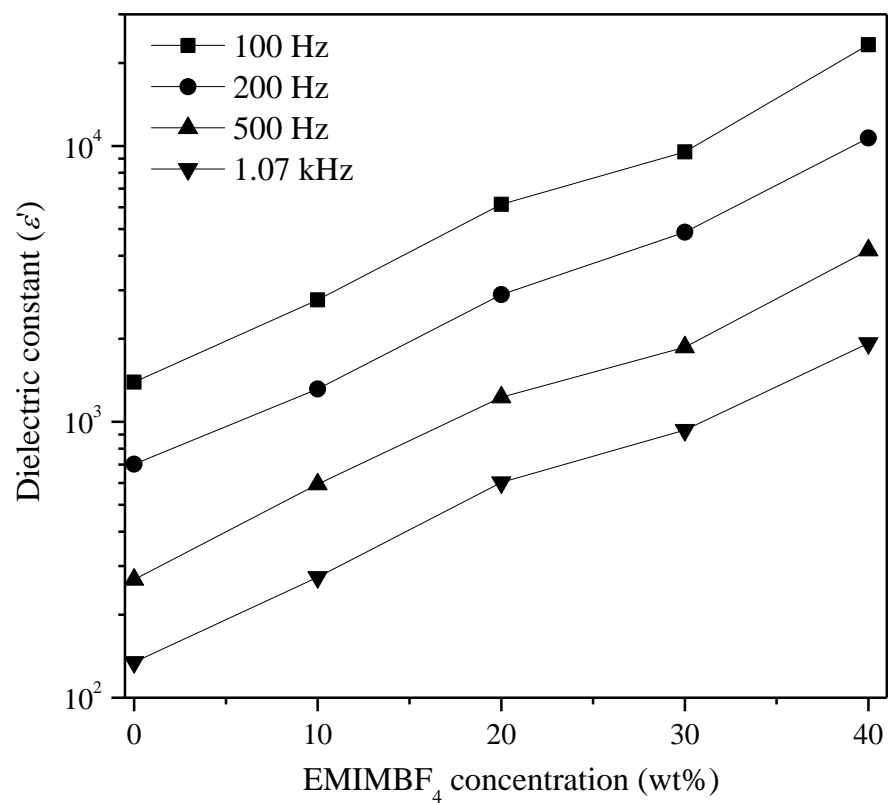


Fig. 8. EMIMBF₄ concentration-dependent dielectric constant at 100 Hz, 200 Hz, 500 Hz and 1.07 kHz for the 85PCL:15LiBF₄+EMIMBF₄ gel polymer electrolyte films

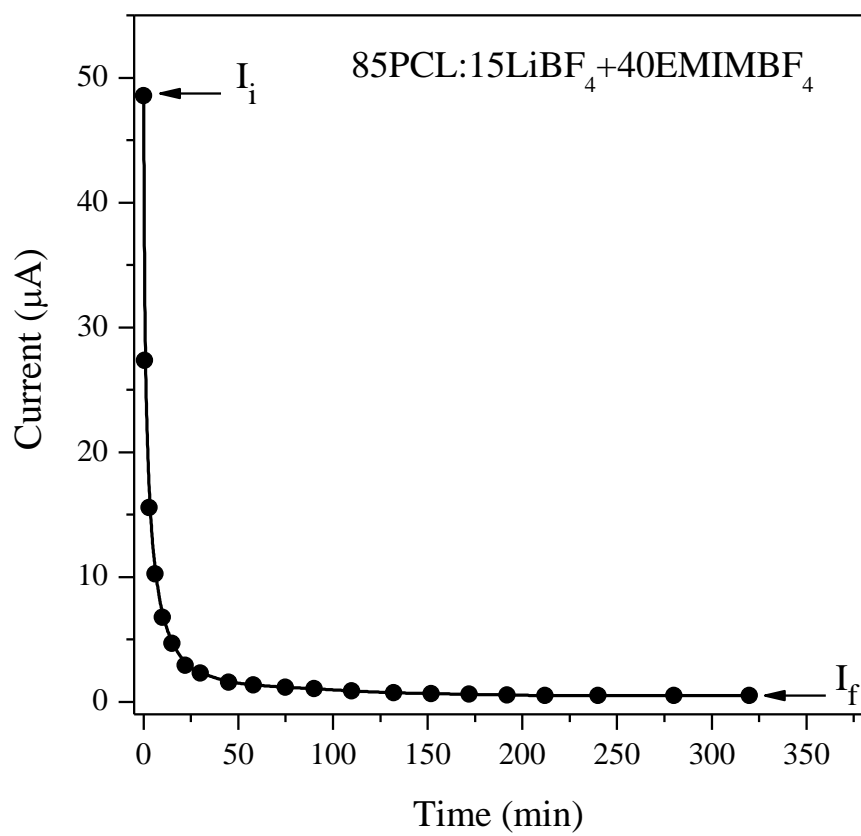


Fig. 9. Polarization current as a function of time for 85PCL:15LiBF₄+40EMIMBF₄ gel polymer electrolyte