

# Temperature dependence of the conductivity of plasticized poly(vinyl chloride)-low molecular weight liquid 50% epoxidized natural rubber solid polymer electrolyte

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**Abstract** Characterizations were carried out to study on a new plasticized solid polymer electrolyte that was composed of blends of poly(vinyl chloride) (PVC), liquid 50% epoxidized natural rubber (LENR50), ethylene carbonate, and polypropylene carbonate. This freestanding solid polymer electrolyte (SPE) was successfully prepared by solution casting technique. Further analysis and characterizations were carried out by using scanning electron microscopy (SEM), X-ray diffraction, differential scanning calorimeter (DSC), Fourier transform infrared (ATR-FTIR), and impedance spectroscopy (EIS). The SEM results show that the morphologies of SPEs are compatible with good homogeneity. No agglomeration was observed. However, upon addition of salt, formation of micropores occurred. It is worth to note that micropores improve the mobility of ions in the SPE system, thus increased the ionic conductivity whereas the crystallinity analysis for SPEs indicates that the  $\text{LiClO}_4$  salt is well complexed in the plasticized PVC-LENR50 as no sharp

crystallinity peak was observed for 5–15% wt.  $\text{LiClO}_4$ . This implies that  $\text{LiClO}_4$  salt interacts with polymer host as more bonds are form via coordination bonding. In DSC study, it is found that the glass temperature ( $T_g$ ) increased with the concentration of  $\text{LiClO}_4$ . The lowest  $T_g$  was obtained at 41.6 °C when incorporated with 15% wt.  $\text{LiClO}_4$ . The features of complexation in the electrolyte matrix were studied using ATR-FTIR at the peaks of  $\text{C=O}$ ,  $\text{C-O-C}$ , and  $\text{C-Cl}$ . In EIS analysis, the highest ionic conductivity obtained was  $1.20 \times 10^{-3} \text{ S cm}^{-1}$  at 15% wt.  $\text{LiClO}_4$  at 353 K.

**Keywords** PVC · LENR50 · Solid polymers electrolyte · Ionic conductivity

## Introduction

Solid polymer electrolytes (SPEs) were first discovered by Fenton, Parker, and Wright (1973) [1] and then extensively studied by Armand (1978) [2] who recognized their unique potential as electrolytes with a “solid solvent.” These materials consist of salts that are dissolved in a solid which serves as a coordinating polymeric solvent [1–3]. In this paper, poly(vinyl chloride) (PVC) and liquid epoxidized natural rubber (LENR50) were used as polymer host for SPE system with ethylene carbonate (EC) and polypropylene carbonate (PC) as plasticizers to enhance the ionic conductivity of the polymer electrolytes. The popular PVC is well known for its excellent miscibility and compatibility with most solvent and plasticizers. Most importantly, PVC possesses superior mechanical properties. This is due to its lone pair of electron from the chlorine atom which can act to stiffen the backbone of the polymer. The lack of mechanical strength was often seen as the main problem face by most of the polymer electrolytes. To overcome this problem, the

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inexpensive and easy processability of PVC was chosen [4]. Besides, PVC can be well solvated with the inorganic salts [5–10]. However, PVC possesses medium dielectric constant ( $\epsilon \approx 3.0$ ) compare to PVdF ( $\epsilon \approx 8.4$ ) [11].

Epoxidized natural rubber (ENR50) has gained numerous attentions from many researches for its distinctive properties of having low glass transition temperature ( $T_g$ ) with good elasticity and adhesion properties [13–15]. In addition, it can provide coordination sites for  $\text{Li}^+$  ions conduction and can produce a great number of charge carriers for ionic transport because it exhibits a lone pair of electrons from the oxygen atom [3]. However, in this paper, we will emphasize mainly on LENR50. LENR50 is an ENR50 modified via photochemical method to produce the low molecular weight liquid epoxidized natural rubber. According to Nair et al. [16], a particular polymer mixture can be made more miscible by reducing the molecular weight of one or both components. This finding is based on the Flory–Huggins theory in which enthalpy gained on mixing polymers is inversely related to their  $M_n$  [16]. Having this assumption, by having lower molecular weight, we expect it to give better property than ENR50 in terms of greater penetration into PVC interstices enabling better solubilization of the PVC segments in the polymer blend of PVC-LENR50-salt system [17–20]. From the point of view of electrochemical applications, PVC-LENR50-based electrolytes have a good prospect in secondary batteries industries as it has good flexibility and mechanical properties for volume changes during cycling process in the battery cell without physical degradation on the interfacial contact, which is often observed in crystalline or vitreous solid electrolytes [2].

In this study, the promising  $\text{LiClO}_4$  salt has been chosen as a dopant for plasticized PVC-LENR50 since it has large anion size, has low lattice energy, exhibits great delocalized charges, and has high energy density that favor ionic dissociation in a solvating polymer. It also has good chemical, electrochemical, and thermal stabilities as well as plasticizing effect which can decrease the crystallinity of the polymer host which makes ionic mobility easier [5]. The dissolution of a salt in a solvent can be explained thermodynamically through Gibbs free energy [1].

In the present work, we had successfully prepared a solid polymer electrolyte consisting of modified low molecular weight rubber LENR50-based PVC- $\text{LiClO}_4$  system with enhancement of plasticizer EC and PC.

## Experimental

### Materials

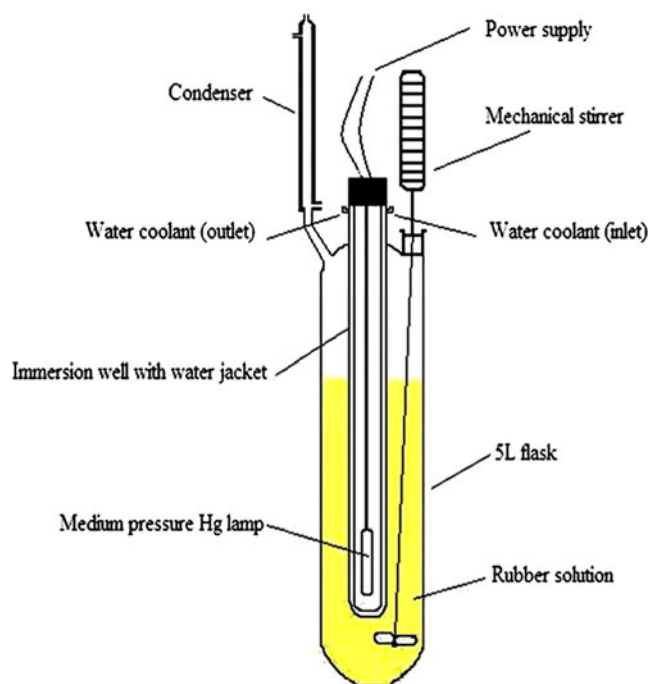
PVC (Aldrich) with an average molecular weight of 97,000 and ENR50 (Guthrie (M) Bhd.) were used in

this work. Lithium perchlorate ( $\text{LiClO}_4$ , purity > 95%) was obtained from Aldrich, while EC and PC were obtained from Fluka. Tetrahydrofuran (THF) was purchased from JT Barker whereas toluene was from R&M Chemical England.

### Sample preparation of LENR50

The rubber solution with 5% wt. was prepared by cutting 250 g of 50% ENR50 into smaller size before putting it into a 5-L straight-sided cylindrical flask which contains 4,750 g of toluene solvent. The cylindrical flask was fitted together with an immersion well, a stirring assembly, and a condenser as shown in Fig. 1. ENR50 was stirred until it was completely dissolved. The ENR50 solution was then irradiated for 50 h with a medium pressure mercury lamp of 400 W which was fitted in the double-walled immersion well made from quartz that allows water cooling from the chiller. The temperature was maintained at 20 °C throughout the process. The depolymerized ENR50 was recovered before using a rotary evaporator to remove the excess solvent until 60% of dried rubber content in the solution was achieved. The temperature of the evaporation process was set at 60 °C. The  $M_w$  of LENR50 before irradiation was 639,661 Da and was reduced to 76,473 Da after it was irradiated for 50 h [17–20].

In the degradation process of ENR50, the chain scission takes place at C–C bond that binds the two isoprene units together. This is due to the resonance energy effect which



**Fig. 1** UV irradiation system

resulted in it being the weakest bond with an energy value of 181 kJ/mol only. It is reported by Dahlan and Abdul Ghani that the liquid form of ENR50 prepared by this technique did not show any significant changes in the absorption peaks of isoprene unit except for the prominent enhanced peak for –OOH and carbonyl groups in the IR. It is suggested that the formation of carbonyl groups occurred as a result of the ring opening of the epoxy group to produce hydroxylated group [17–20].

#### Sample preparation of SPE

PVC powder with a weight of 0.9 g was dissolved in 60 mL of THF and stirred using a magnetic stirrer until all PVC was completely dissolved. LENR50 with a weight of 3.5 g which contains 2.1 g of DRC was introduced into the PVC solution and stirred for 24 h to form a homogenous solution. EC and PC were then added into the solution before 5% wt. of  $\text{LiClO}_4$  was introduced into the mixtures solution. The solution was continually stirred for another 24 h. This homogenous solution was casted into a finely cleaned petri dish before allowing it to evaporate in a fume hood at room temperature for a day. After appropriate amount of THF solvent was dried off, the sample was further dried in a vacuum oven at 50 °C and 0.2 atm for 24 h to further remove any residue and solvent. The dried film was obtained after THF solvent had completely evaporated. The film was then peeled off from the petri dish. These steps were repeated for SPEs with 10% to 30% wt.  $\text{LiClO}_4$ . This process produced a mechanically stable and a free-standing electrolytes film.

#### Sample characterization

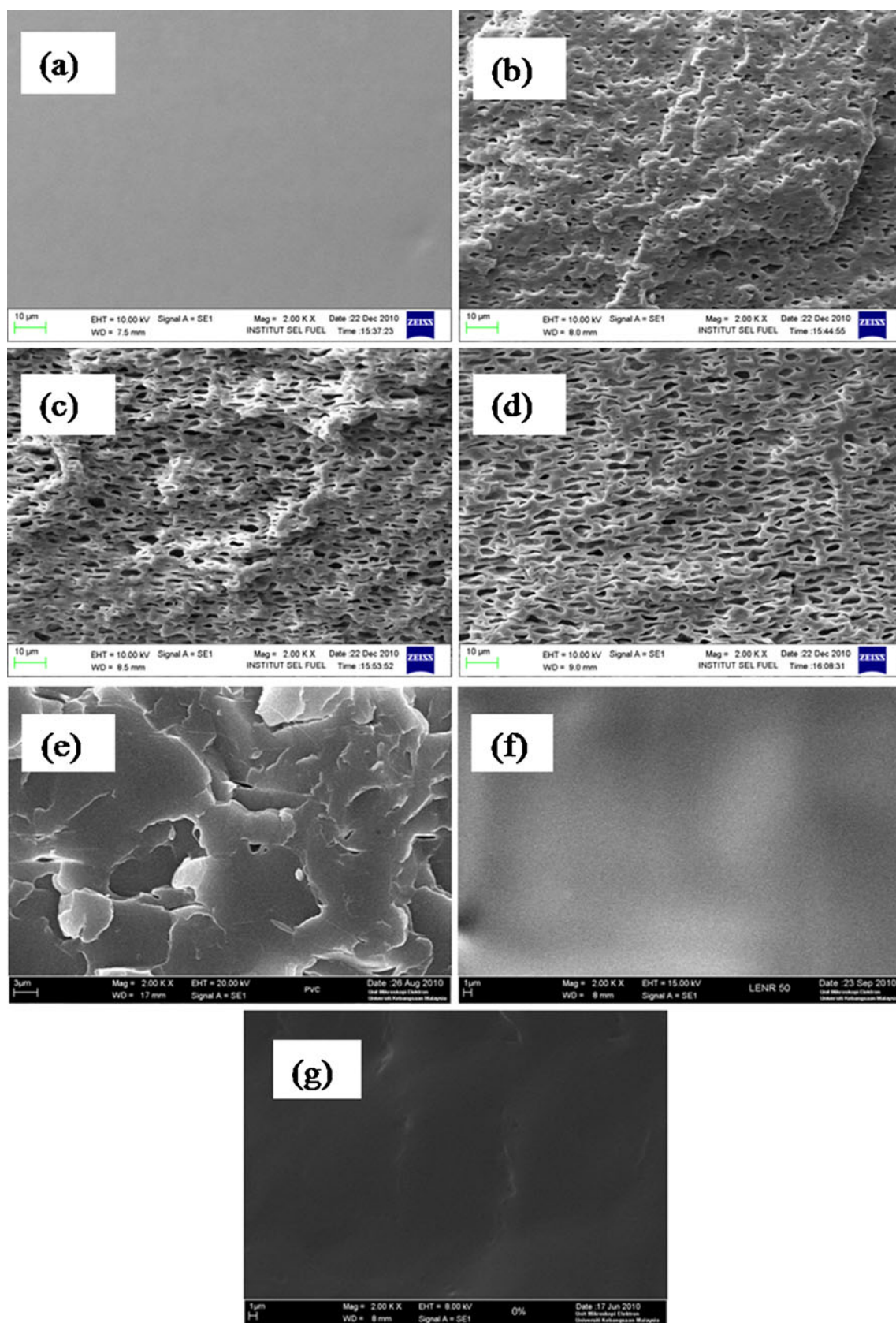
The morphological studies on the fractured surfaces of the polymer electrolyte samples were performed using scanning electron microscopy (SEM) with 2,000× magnification at 25 kV electron beam. X-ray diffraction technique was conducted by Siemens model D5000 at room temperature to determine the crystalline phase of the polymer electrolyte samples. X-ray diffraction measurements were conducted to examine the nature of the crystallinity of the polymer with respect to  $\text{LiClO}_4$  salt and to investigate the occurrence of complexation within 5° to 60°. The X-ray source used was  $\text{CuK}\alpha$  with a wavelength of 1.5418 Å and a diffraction angle of  $2\theta$  ranging from 2° to 60°. Thermal analysis was performed using differential scanning calorimeter (DSC) model Mettler Toledo 822. An investigation on the behavior changes in thermal properties of SPEs with respect to lithium salt concentrations was performed by DSC in a temperature range of –60 to 120 °C. The samples were heated under nitrogen gas with a heating rate of 10 °C/min interval.  $T_g$  of the samples which is midpoint of the endothermic

reaction was evaluated from the STARE software. Fourier transform infrared (ATR-FTIR) analysis was performed on polymer-based and lithium salt using the Perkin Elmer Spectrum 2000 in the range of 4,000 to 500  $\text{cm}^{-1}$  with its scanning resolution of 4  $\text{cm}^{-1}$ . Analysis of IR spectrum using ATR-FTIR type was performed on SPEs to study the changes of vibration energy of covalent bonds in the polymer host and also the interactions occurred when the salts were incorporated into the system. The ionic conductivity measurement was performed by alternate current impedance spectroscopy using a high frequency response analyzer (HFRA Solartron 1256, Schlumberger) in the frequency range of 0.1 to 1 MHz. The electrolyte films were sandwiched between two stainless steel electrodes with a surface contact area of 2.0  $\text{cm}^2$  and mounted onto the holder. From the Cole–Cole plots, the bulks resistance,  $R_b$  ( $\Omega$ ), of the samples was determined with ZView software. The conductivity was calculated based on the equation  $\sigma = l / R_b A$ , where  $l$  is the film thickness (cm) and  $A$  ( $\text{cm}^2$ ) is the effective contact area of the electrolyte and the electrode. Same procedures were applied for conductivity dependence temperature measurement which conducted at a temperature range of 30 to 140 °C at 10-°C intervals. The samples were heated in the thermostatic oven ANDO TO 19. The conductivity,  $\sigma$ , and the dependence on temperature,  $T$ , is given by the Arrhenius equation:  $\sigma = \sigma_o \exp(-E_a / kT)$  where  $\sigma_o$ ,  $E_a$ , and  $k$  represent preexponential factor, activation energy, and Boltzmann constant, respectively. The values of  $\sigma_o$  and  $E_a$  can be computed from the interception of y-axis and from the slope of the plotted graph of  $\log \sigma$  versus  $1,000/T$ , respectively.

## Result and discussion

#### Scanning electron microscopy studies

Figure 2 represents the SEM micrographs taken from the cross-sectional area of SPEs with different concentrations of  $\text{LiClO}_4$  salts, pure PVC, and pure LENR50. In Fig. 2e, the cross-sectional area of PVC was rough with cracked surfaces. In contrast to LENR50 that was shown in Fig. 2f, the surface was relatively smooth and clean. When PVC was blended together with LENR50, the surfaces of PVC were greatly improved as no crack or brittleness surfaces were found as shown in Fig. 2g. Moreover, LENR50 has better miscibility than ENR50 owing to its smaller molecular size. LENR50 contributes larger interphasing area and higher interaction with PVC [12]. In addition, the physical properties PVC-LENR50 blends also improved as PVC and LENR50 compensate for each other's weaknesses. PVC provides better mechanical strength whereas LENR50 enhanced the tear strength, adhesion, and elasticity of the



**Fig. 2** SEM micrograph of **a** SPE 0% wt.  $\text{LiClO}_4$ , **b** SPE 5% wt.  $\text{LiClO}_4$ , **c** SPE 15% wt.  $\text{LiClO}_4$ , **d** SPE 30% wt. of  $\text{LiClO}_4$ , **e** pure PVC, **f** pure LENR50, and **g** PVC-LERN50



system [3, 10, 17, 18]. These properties appeared to be important for application in solid polymer battery lithium as discharging and charging process will result in volume change of the electrolyte [2]. Besides, it appeared that upon addition of EC and PC, the surface was smoother and no agglomerates were found as shown in Fig. 2a. We can conclude that PVC-LENR50-EC/PC blend was miscible and compatible.

Figure 2b–d represents the cross-sectional views of PVC-LENR50-EC/PC host doped with 5%, 15%, and 30% wt.  $\text{LiClO}_4$ , respectively. Interestingly, micropores were observed in SPEs complexes structural built when salts were introduced. This phenomenon was due to the complex process of interaction between the solvent, lithium salt, and polymer during the evaporation (drying process) in which it was kinetically controlled by the relative rate of evaporation of the compounds [17, 21, 22]. It was suggested that the existing porosity in the SPEs matrix was due to subsequence of repulsive forces between anions group and polymer host [23]. Nevertheless, the formation of micropores was proved to enhance the ionic conductivity by providing more pathways in ion transportation properties. Although the porosity enhances the ionic conductivity; however, the ionic conductivity dropped after 15% wt.  $\text{LiClO}_4$  was introduced. This was because the presence of high concentration of lithium salt will favor the formation of ion pairs in which these

ion pairs carried no charges [2]. As we observed, there were more bright spots in Fig. 2d than other SPEs. This indicates that it is caused by formation of salts. This was proven by X-ray diffraction (XRD) results which showed that crystalline peaks occurred after 15% wt.  $\text{LiClO}_4$  was introduced.

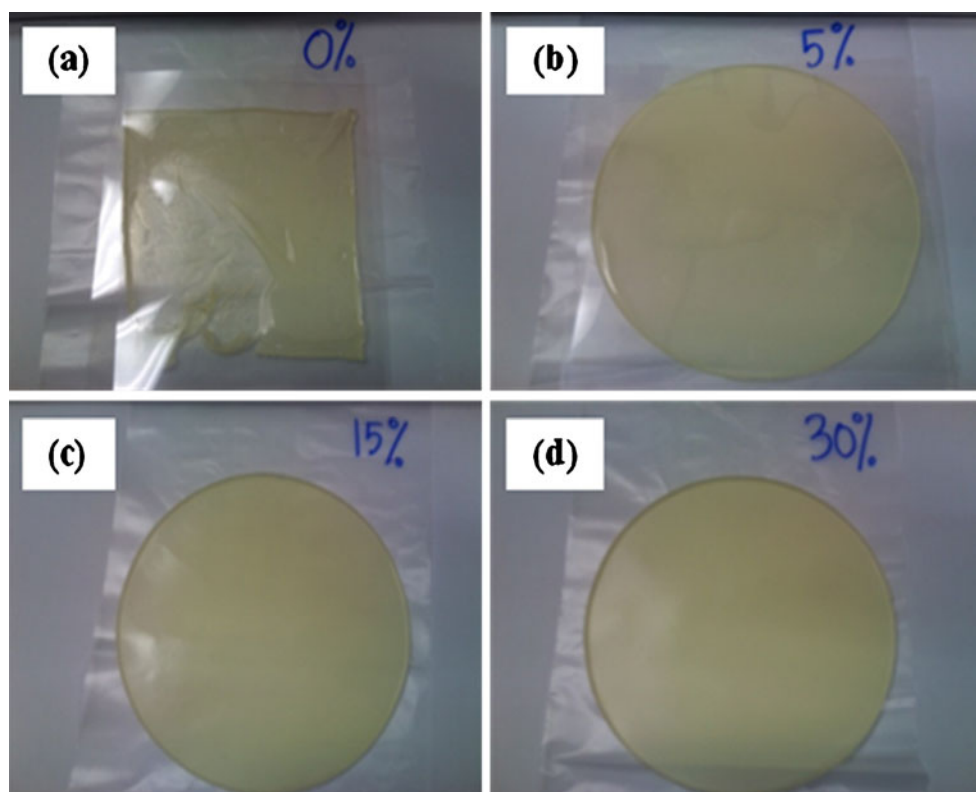
Figure 3 shows the smooth thin films of SPEs with variation in salt concentration. It was worth noted that as  $\text{LiClO}_4$  salt increased, the transparency of the SPEs was reduced. Physically, the SPE became less sticky, and the softness decreased too when more salts were introduced compare with nonsalt SPE. The softness of the SPEs decreased because the  $T_g$  increased, and it is discussed later on in DSC section.

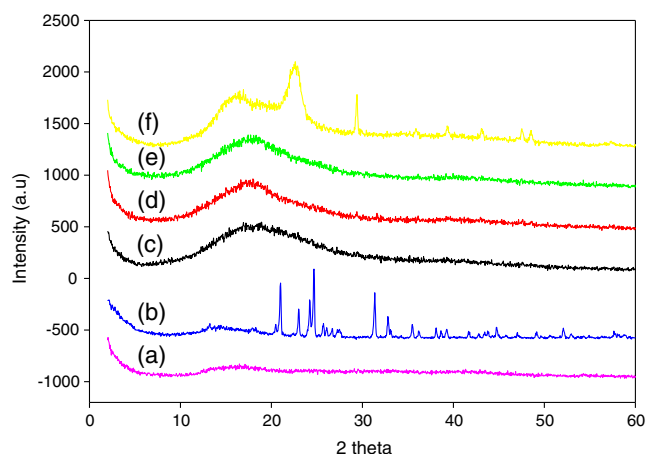
#### XRD analysis

The diffraction patterns of SPEs were shown in Fig. 4. From Fig. 4g, no sharp peak was observed for pure PVC except for a single broad peak. The broad peak is referred as “amorphous hump” and is a typical characteristic of an amorphous material. This implies that PVC is a fully amorphous polymer [21].

From Fig. 4c–f, only a clear single hump in the region of  $10^\circ$  to  $26^\circ$  was observed upon incorporating lithium salt. The absence of sharp crystalline peaks shows that the

**Fig. 3** The SPEs samples of PVC-LENR50 (30/70)-EC/PC (50/50) with **a** 0% wt.  $\text{LiClO}_4$ , **b** 5% wt.  $\text{LiClO}_4$ , **c** 15% wt.  $\text{LiClO}_4$ , and **d** 30% wt.  $\text{LiClO}_4$





**Fig. 4** Typical diffraction patterns for **a** pure PVC and **b** pure  $\text{LiClO}_4$  salt and SPEs with variation salt contents at **c** 0% wt., **d** 5% wt., **e** 15% wt., and **f** 30% wt.  $\text{LiClO}_4$

lithium salt was well complexed in the amorphous polymer host system. In the amorphous region, the barrier energy is low and therefore favors the ionic diffusivity of lithium salt. Besides, amorphous polymer has better flexibility backbone and therefore exhibits better mobility and movements in local chains of polymer. In fact, an ionic conductivity for a SPE is influenced by the segmental motions of polymer local chains through making and breaking the coordination sphere of the solvated ions. In addition, this motion process also provides larger space (free volume) in which the ions may diffuse under the influence of the electrical field [25].

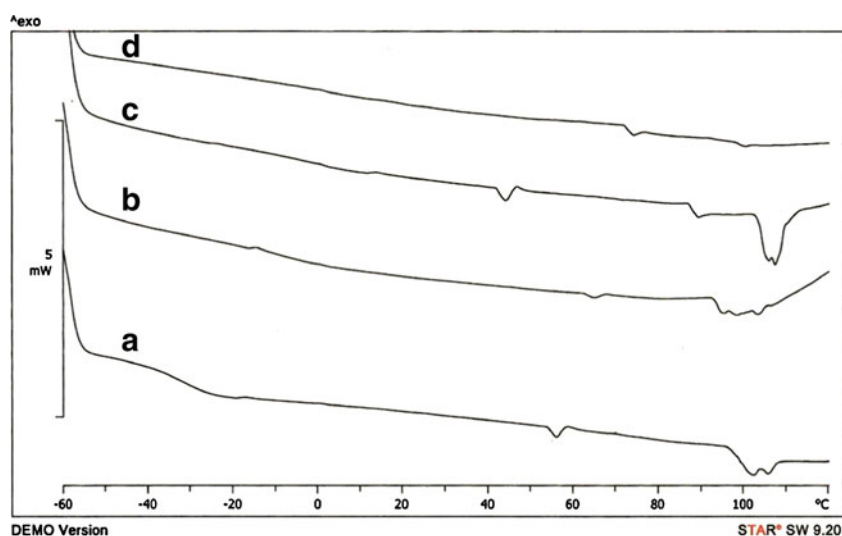
However, the crystalline peaks were only observed at the addition of 30% wt.  $\text{LiClO}_4$ . This happened when the concentration of salt was too high in the complexes system; ion association of  $\text{Li}^+$  and  $\text{ClO}_4^-$  tends to occur which will decrease the ionic conductivity. As discussed by Wanchart

et. al., at concentration of salt higher than the solubility limit of the system, crystalline complexes will form [24]. According to Binod et al., a faster ionic transport takes place in the amorphous phase in which the conductivity is about two to three orders of magnitude greater as compared with the crystalline phase [26].

#### Thermal analysis

The thermal analysis results were shown in Fig. 5 and Table 1. According to Fig. 5, it was observed that  $T_g$  increased with the addition of salts. However, the lowest  $T_g$  was achieved at 41.6 °C with the incorporation of 15% wt. salt which was the optimum value for ionic conductivity. The changes in the thermal properties indicate the complex interaction between lithium salt and polymer host.  $\text{Li}^+$  ions tend to interact with electron-rich coordinating groups such as ether and carbonyl groups via transient cross-linkage bonds [24]. The cation–oxygen and cation–chlorine binding energy, which is the driving force for salt dissolution, contributes to the increasing barrier to rotation of the polymer segments. Subsequently, the energy barrier for segmental movement in polymer increases. Therefore, this will reduce the flexibility of polymer backbone and caused the rise in  $T_g$  value for the complexes [21, 23]. Moreover, when the salt dissolves in polymer and dissociates into ions, it generates carrier ions and at the same time increases the viscosity. These two results have opposite effects on conductivity in which the former increases the conductivity, while the latter decreases the conductivity [23]. This phenomenon is due to salt ions acting as transient cross-linking agents that increase the  $T_g$  and thereby decrease the ionic mobility. Other than salt effect on increasing  $T_g$  value, Nair et al. discussed that PVC and ENR50 can form self-crosslinkable blends. The

**Fig. 5** DSC thermograms of PVC-LENR50 (30/70)-EC/PC (50/50) doped with variation concentration of  $\text{LiClO}_4$  **a** 0%, **b** 5%, **c** 15%, and **d** 30%



**Table 1** Transition glass temperature of PVC-LENR50 (30/70)-EC/PC (50/50)-LiClO<sub>4</sub>

Salt contents by weight percentage (%)	$T_g$ (°C)	
	1st	2nd
0	53.8	–
5	62.5	–
15	41.6	90.5
30	71.8	102.0

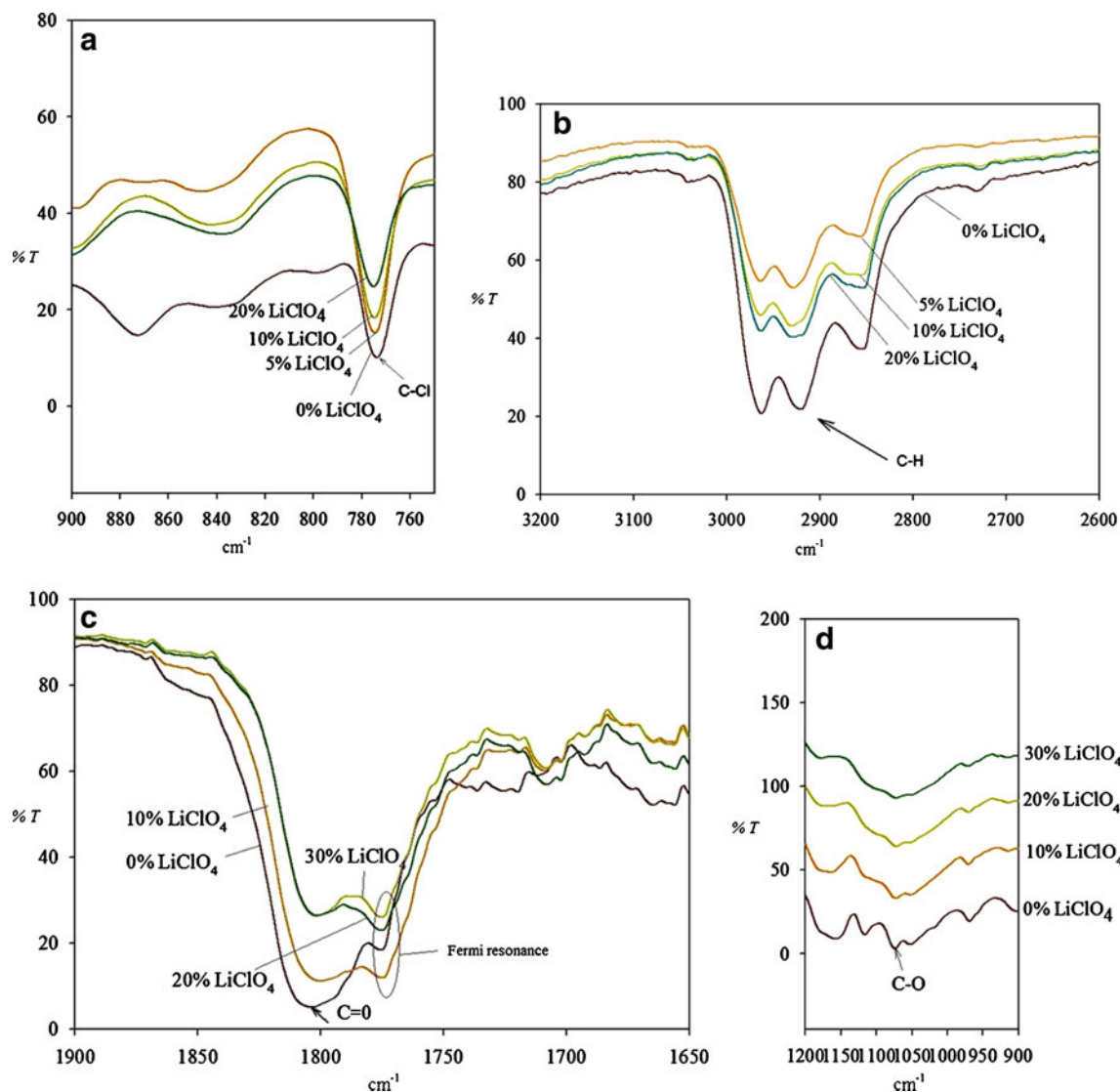
introduction of oxirane group gives a stiffer polymeric plasticizer compare with those pendent active groups [16].

Furthermore, it is known that additives such as Li<sup>+</sup>, Fe<sup>2+</sup>, and Fe<sup>3+</sup> ions were regarded as active dechlorination agents for PVC and its derivatives. In some cases, anions such as ClO<sub>4</sub><sup>−</sup>, Γ<sup>−</sup>, and SO<sub>4</sub><sup>−</sup> can accelerate the thermal decomposition of PVC including drying process when solid polymer

electrolyte is produced from solutions [27]. Eventually, dechlorination can also promote the cross-linking between the polymer segments that leads to the increase in  $T_g$  when more salts were doped in the polymer electrolyte [23]. In addition, only one distinct peak was observed for the SPEs doped with less than 15% wt. LiClO<sub>4</sub> which indicates the homogeneous behavior of the polymer electrolytes. However, two peaks exist when incorporating 15% and 30% wt. LiClO<sub>4</sub>. It is suggested that the increment salt caused significant repulsion forces with the polymers due to the increasing ClO<sub>4</sub><sup>−</sup> anion and subsequently promotes phase separations.

#### ATR-FTIR analysis

Figure 6 shows the FTIR spectra for C–Cl, C–H, C=O, and C–O groups of SPEs. Among the bands observed is the

**Fig. 6** FTIR spectra for **a** C–Cl, **b** C–H, **c** C=O, and **d** C–O of SPEs

functional group of C–Cl stretching at  $775\text{ cm}^{-1}$  for aliphatic PVC. When the salts were added into the SPEs, the intensity peak of the band was decreased and shifted to  $773\text{ cm}^{-1}$  as shown in Fig. 6a. This is clearly an evident that complexation had occurred between functional group C–Cl and  $\text{Li}^+$  ions.

In Fig. 6b, stretching C–H spectrums were observed at 2,963, 2,923 and  $2,860\text{ cm}^{-1}$ . It is interesting to note that the intensity of the peaks decreased proportional to the concentration of lithium salts. The band of the functional group C=O stretching from LENR50, EC, and PC was found at  $1,802\text{ cm}^{-1}$  as shown in Fig. 6c. Similarly, the intensity of the peak was altered to lower intensity upon adding lithium salts. It is worth noting that the sharp intensity peak of C=O from EC and PC has been split into two smaller peaks, which are attributed to Fermi resonance of the C=O stretching mode with an overtone of the ring breathing mode and the existence of the short-range ordering of the molecular orientation that originated from the dipole–dipole coupling of two EC molecules. Fermi resonance occurred due to the coupling of the two fundamental vibrational modes or the interaction between fundamental vibrations and overtones [28].

The absorption peak at  $1,073\text{ cm}^{-1}$  was assigned to asymmetric stretching C–O functional group. C–O group was originated from structural of EC, PC, and LENR50. However, the intensity became weak and disappeared when salts were added which was shown in Fig. 6d. These shifts in frequencies, modification of a single into doublet, and disappearance of some peaks on blending electrolytes lead to the occurrence of complex formation between polymer plasticizers.

#### Ionic conductivity analysis

Table 2 shows the relationship between the concentration of lithium salts, bulk resistance, and ionic conductivity of SPEs at room temperature. Overall, the bulk resistance varies with the concentration of  $\text{LiClO}_4$ . It is observed that bulk resistance decreased with addition of 0% to 15% wt.  $\text{LiClO}_4$  salts. However, further addition of  $\text{LiClO}_4$  salt caused the bulk resistance to increase. The highest ionic conductivity at

$8.0 \times 10^{-8}\text{ S cm}^{-1}$  is obtained at 15% wt.  $\text{LiClO}_4$  which has the smallest value of bulk resistance at  $2.3 \times 10^5\ \Omega$ . The increase in the ionic conductivity after the introduction of  $\text{LiClO}_4$  salt into the electrolyte system was due to the increasing charge carriers in the system. This can be shown by the equation  $\sigma = ce(u_+ + u_-) = c\Lambda$  in which  $\sigma$  is the conductivity of electrolytes,  $\Lambda$  is the molar conductivity,  $c$  is the salt concentration,  $e$  is the charge of an electron, and  $u_+$  and  $u_-$  represent the ion mobility. As the number of charges increases, the ionic conductivity also increases [1, 22].

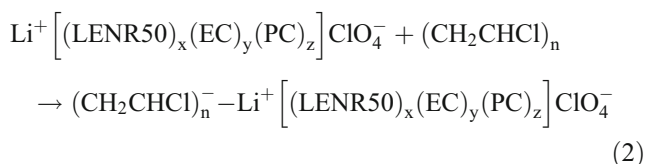
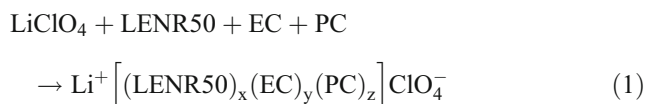
Previous researches reported that plasticizer such as EC exhibit high dielectric constant which can increase the number of mobile ions by weakening the Coulombic force between the anions and cations of the salt [29]. Besides, plasticizer creates and promotes more free volume in the electrolyte system, thus decreases the viscosity of the electrolyte making the mobility of ions became easier. Furthermore, the increased in ionic conductivity of the SPEs was also attributed to the large volume of  $\text{ClO}_4^-$  ions which may elongate the pitch of PVC spiral structure and thus provides a bigger transfer space for  $\text{Li}^+$  [30]. Moreover, the low molecular weight of LENR50 with shorter chains than ENR50 was thought to have played the same role as “plasticizer” that reduces the viscosity of the PVC chains and hence increases the chain mobility. On the other hand, PVC may act as a “mechanical stiffener” for LENR50. Previously, the ENR50 was reported to be used as plasticizer in PVC-ENR50 and PEO-ENR50 blends which were found to reduce the stiffness of the PVC and PEO [3, 9, 15]. However, beyond this optimum concentration of  $\text{LiClO}_4$  salt, the ionic conductivity decreases. This implies that ion association likely occurred in the electrolyte system. Ion association caused the number of free ions to decrease which leads to the lower ionic conductivity values [31]. This can be explained by the fact that at extreme low salts concentrations, the salts exist in the form of isolated  $\text{Li}^+$  and  $\text{ClO}_4^-$  ions. When the concentration of salt increased, mutual interactions between ions are sufficiently strong to promote the formation of ion pairs, which are in equilibrium with the free ions. Since the ions pairs carry no charge, the conductivity

**Table 2** Ionic conductivity of PVC-LENR50 (30/70)-EC/PC (50/50) doped with variation concentration of  $\text{LiClO}_4$  salts

Weight percentage of $\text{LiClO}_4$	Thickness (cm)	Resistivity bulk, $R_b$ ( $\Omega$ )	Ionic conductivity, $\sigma$ ( $\text{S cm}^{-1}$ )
0	0.03	$6.59 \times 10^5$	$1.96 \times 10^{-8}$
5	0.03	$4.67 \times 10^5$	$2.66 \times 10^{-8}$
10	0.03	$4.32 \times 10^5$	$2.88 \times 10^{-8}$
15	0.04	$2.31 \times 10^5$	$7.99 \times 10^{-8}$
20	0.03	$2.89 \times 10^5$	$4.66 \times 10^{-8}$
25	0.03	$4.12 \times 10^5$	$3.02 \times 10^{-8}$
30	0.03	$5.90 \times 10^5$	$1.94 \times 10^{-8}$



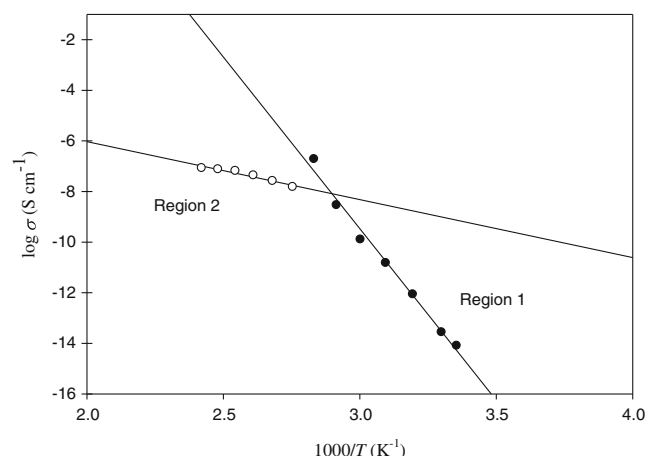
per unit salt concentration will drop as observed in Table 2. The formation of the SPE complex is described below [1, 3, 30, 32]:



Another possible reason is that the excessive salt will also increase the transient cross-linking in the electrolytes and thus reduces its chain mobility. This is further proven by the results in DSC. Besides, Xuping et al. noted that when the content of salt increases, the amount of  $\text{ClO}_4^-$  will also increase in the mean time too, which will occupy the space of PVC network structure and thus blocks the diffusion of lithium ions [30].

The XRD and DSC results also confirmed that amorphous regions did achieve better ionic conductivity compare to crystalline and partial-crystalline regions [21]. We can conclude that the salt affects the overall ionic conductivity of the SPE through formation of crystalline phases and intramolecular cross-linkages as well as degree of dissociation number of charge carriers [2]. However, the conductivity did not increased significantly. From the IR results, we suggest that lithium salt does not interact chemically much with the polymer blends as only slightly peak shifting was observed at C–Cl.

Figure 7 shows the dependence of conductivity on the temperature by the Arrhenius plot for PVC-LENR50-EC/PC doped with 15% wt. of lithium salts. The relationship shows



**Fig. 7** Variation of conductivity of PVC-LENR50 (30/70)-EC/PC(50/50)  $\text{LiClO}_4$  (15% wt.) polymer electrolytes with temperature

that the plot is linear indicating the electrolyte is following the Arrhenius plot. Therefore, the value of  $\sigma_0$  and  $E_a$  can be estimated from the plot. Since the conductivity–temperature data follow Arrhenius behavior, the nature of cation transport is quite similar to that in ionic crystals, where ions jump into neighboring vacant site [33]. Interestingly, the overall plot can be divided into two parts of the Arrhenius plots. The  $E_a$  for region 1 and region 2 are 2.65 and 0.46 eV, respectively. The  $\sigma_0$  for region 1 and region 2 are  $1.0 \times 10^4$  and  $1.0 \times 10^{-6} \text{ S cm}^{-1}$ , respectively. This could well indicate that electrolyte undergoes changes in chemical and physical properties at temperature around 353 K. According to the DSC result in Fig. 5,  $T_g$  for low molecular rubber-based electrolyte doped with 15% wt.  $\text{LiClO}_4$  is at around 40 and 90 °C (313 and 363 K) in which electrolyte starting to exhibit rubberlike phase from solid phase as polymer chains gained enough energy to move more freely. The increasing conductivity with temperature can be linked to the decrease in viscosity and, hence, increased the chain flexibility of the electrolyte. As the temperature increases, the mobility and the dissociation rate of  $\text{Li}^+$  ion also increase, thus improving the conductivity of the electrolyte. The increment in temperature provides an increase in free volume and segmental mobility [11]. These two entities then permit free charges to hop from one site to another, thus increasing the conductivity. The conductivity increases as temperature indicates that more ions gained kinetic energy via thermally activated hopping of charge carriers between trapped sites, which is temperature dependent. Moreover, the sharp increase of conductivity at temperature around 343–353 K is attributed by the large heat energy absorbed by the sample and thus induced the conductivity. Meanwhile, Noor et al. had suggested that the value of  $E_a$  is due to the energy required to provide a conductive condition for the migration of ions [3]. This is because the activation energy is a combination of the energy of the charge carrier creation (defect formation) and the energy of the ion migration that can be evaluated by a linear fit of the plot. The low activation energy for the lithium ion transport was due to the completely amorphous nature of the polymer electrolytes that facilitate the fast  $\text{Li}^+$  ion motion in the polymer network. The completely amorphous nature also provided a bigger free volume in the polymer electrolyte system upon increasing the temperature [34].

## Conclusions

Solid polymeric electrolyte of PVC-LENR50 (30/70)-EC/PC (50/50) with function of  $\text{LiClO}_4$  salt concentration was successfully prepared by solution casting technique. The highest ionic conductivity obtained is  $2.05 \times 10^{-7} \text{ S cm}^{-1}$  at 15% wt.  $\text{LiClO}_4$  salt. Although PVC-LENR50 (30/70) with plasticizers blends were miscible and compatible, it

appeared that the ionic conductivity of the SPEs were still quite low at ambient temperature considering that the SPEs were high in bulk resistance. This is because the PVC and LENR50 can form self-crosslinkable blends. Besides, it was proposed that PVC has the main contribution to the high bulk resistance outcomes because the excessive PVC adulteration will increase the dehydrochlorination process, thus promoting the cross-linking between the polymer segments. Subsequently, this leads to insufficient flexibility of polymer chain and impedes the ion transportation. In thermal studies, the  $T_g$  increased when the salt content increased because more cross-linkage were produced via coordination bonds between cations and polymers. The SEM studies showed that PVC, LENR50, and plasticizers were well miscible as suggested by other researchers. This was further proved by XRD results which show that salts were fully complexed with the polymer host as no crystalline peaks were observed. However, beyond 15% wt.  $\text{LiClO}_4$ , crystalline peaks were observed due to association of ions. It also reveals that the SPEs with lithium salts produce almost consistent sizes and well-distributed micropores. The micropores aid in the mobility of the ions in the system complexes. Results of the ATR-FTIR proved that complexation occurred between  $\text{Li}^+$  ions and functional groups of C–Cl and C–O–C as well as C=O. The highest conductivity achieved at 80 °C is  $1.20 \times 10^{-3} \text{ S cm}^{-1}$ , and the conductivity dependence temperature is Arrhenian.

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