LiClO$_4$ Salt Concentration Effect on the Properties of PVC-Modified Low Molecular Weight LENR50-Based Solid Polymer Electrolyte

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ABSTRACT: A work was carried out on a solid polymeric electrolyte system comprising blends of poly (vinyl chloride) and liquid 50% epoxidized natural rubber (LENR50) as a polymer host with LiClO$_4$ as a salt and prepared by solution casting technique. In this paper, the main study was the effect of LiClO$_4$ salt concentration on the electrolyte properties. The effect of the salt on the electrolyte properties was characterized and analyzed with impedance spectroscopy (EIS), X-ray diffraction (XRD), differential scanning calorimeter (DSC), and scanning electron microscopy (SEM). The EIS result showed that highest ionic conductivity was obtained at 30 wt % salt with a value of 2.3×10^{-8} S cm^{-1}. The XRD results revealed that the LiClO$_4$ salt was fully complexed within the polymer host as no sharp peaks were observed. However, above 30 wt % of salt, some sharp peaks were observed. This phenomenon was caused by the association of ions. Meanwhile, DSC analysis showed that T_g increased as the salt content increased. This implied that LiClO$_4$ salt had interaction with polymer host by forming coordination bond. The morphologies' studies showed that good homogeneity and compatibility of the electrolyte were achieved. Upon the addition of the salt, formation of micropores occurred. It was noted that micropores which aid in mobility of ions in the electrolyte system has increased the ionic conductivity. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2227–2233, 2012

Key words: PVC; LENR50; LiClO$_4$; ionic conductivity; solid polymeric electrolyte; glass transition

INTRODUCTION

In recent years, there has been an intensified research and study on all solid-state ionic conductors such as fast/superionic conductors, insertion compounds, polymer electrolytes as well as electrochromic devices. One of the keen interests is to develop solid electrolytes especially solid polymer electrolyte (SPE) because of its wider applications in supercapacitors, electric vehicles (EV), high vacuum electrochemistry, sensors, modified electrode, electrochromic windows, thermoelectric generators, and fuel cells.[1,2] However, SPE was given more attentions in application of secondary lithium ion batteries.

SPEs are expected to replace the conventional liquid electrolyte in batteries since liquid electrolytes have several inevitable drawbacks such as corrosion caused by the powerful solvent leakage that might react with seals or containers of the batteries and the production of harmful gas during operation. However, the SPE-based batteries can be packaged in low-pressure container because of the absence of gas formation and of any significant vapor pressure. In term of design, they can be configured in almost any shape because of the flexibility of the materials used. They exhibit a wider electrochemical and thermal stability as well as low volatility. Other advantages are viz. light in weight, thin, high energy density, better mechanical strength, and high automation process.[1–5]

After more than 30 years since the ionic conducting polymer electrolytes were first suggested by Fenton and Wright in 1973,[6] SPEs systems still face the same particular problem of having low ionic conductivity at ambient temperature.[4,7,8] To overcome this problem, several approaches have been made to improve the conductivity such as using different preparation methods; polymer blending; *in situ* thermal crosslinking; introducing the inorganic compound fillers such as ZnO, ZrO, SnO$_2$, Al$_2$O$_3$, TiO$_2$, NiO and many more into SPE system; irradiating

electrolytes with gamma irradiation, UV irradiation; binary salts system; and adding of plasticizers (EC and PC) that have been reported by many researchers.[5,8–16] Among all these techniques, polymer blending is considered the most feasible technique as it can complement with advantages of other techniques and also enhances the electrical as well as physical properties of polymer electrolytes.[17–19] The mixing of different polymers has revealed a new realm of technically important material as their properties can be altered by varying the composition of the polymer blends. Although a large number of combinations of polymers are possible, relatively few lead to a totally miscible system. A blend of two components is classified miscible, thermodynamically, if the Gibbs free energy of the mixing is negative.[20,21]

In this work, poly (vinyl chloride), PVC was used since processibility is easy, inexpensive, and exhibits good mechanical properties. In fact, it is well known that PVC can excellently form miscible and compatible system with various low or high molecular weight polymers which act as plasticizers and yet still preserve good mechanical strength after blends.[16,22] Scientifically, PVC was a popular choice as polymer host for electrolyte due to its lone pair electrons at the chlorine atom in which inorganic salts can be solvated.[12,19,23] Recently, much attention was also given to modified rubber such as ENR and MG49. ENR was known since 1922 but only became commercially available in the past two decades.[24] Epoxidation of natural rubber produces a random copolymer between isoprene and epoxidized isoprene units. This modified rubber has a lone pair of electrons from the oxygen atom that coordinate with the lithium salt, which provides coordination sites for Li^+ ion conduction and will produce a great number of charge carrier for ionic transport.[4,9,15] The distinctive characteristics of modified natural rubber such as low T_g, soft elastomeric at room temperature, and good elasticity and adhesion properties will help improving the ionic conductivity of the electrolytes.[6] It has attributed to oil resistance, reduced air permeability, damping and wet grip. Contrary to PVC, ENR50 has good mechanical properties of straining induced crystallization.[21,24,25] It is expected that PVC would impart high tensile strength and good chemical resistance while ENR acts as a permanent plasticizer for PVC inducing good tear strength and enhancing resistance against hydrocarbon oils.

Here, we had further improved and modified the properties of ENR50 by irradiation with UV via photochemical reaction to reduce the molecular weight to form liquid 50% epoxidized natural rubber (LENR50). The reduced molecular weight was expected to give better miscibility with PVC as well as introducing a highly flexible copolymeric unit into the structure of polymer blends. This is explained by the fact that rubber with lower chain length provides greater penetration onto PVC interstices enabling better solubility of the PVC segments.[13,14,20,26] In this work, we have successfully prepared a solid polymer electrolyte consisting of modified low molecular weight rubber LENR50 in PVC–LENR50 (30/70)–$LiClO_4$ system.

EXPERIMENTAL

Materials

PVC (Aldrich) with average molecular weight of 97,000 and ENR50 (Guthrie (M) Bhd.) were used in this work. Lithium perchlorate ($LiClO_4$, purity > 95%) was obtained from Aldrich. Tetrahydrofuran (THF) was purchased from JT Barker whereas toluene was from R and M Chemical England.

Sample preparation of LENR50

Before the rubber solution of 5% was prepared, 250 g of 50% epoxidized natural rubber (ENR50) was cut into smaller size and put into 5 L of straight-sided cylindrical flask which contained 4750 g of toluene solvent. The cylindrical flask was fitted together with an immersion well, a stirring assembly, and a condenser. The ENR50 was stirred until it is completely dissolved. The ENR50 solution was then radiated for 50 h with a medium pressure mercury lamp of 400 W which was contained in the double-walled immersion well made from quartz allowing water cooling by a chiller. The temperature was fixed at 20°C throughout the process. The depolymerized ENR50 was recovered first and concentrating the rubber solution using a rotary evaporator at 60°C until 60% of dried rubber contained (DRC) in the solution was achieved. The M_w of LENR50 before irradiation was 639,661 Da and after irradiation for 50 h was 76,473 Da.[13,14,26] Figure 1 shows the degradation of ENR50 upon irradiation with UV light while Figure 2 shows the proposed structure and mechanism routes for irradiation of LENR50. In the process of degradation of ENR50, the chain scission takes place at C–C bond which binds the two isoprene units together. This was because of the resonance energy which results in it being the weakest bond with energy value of 181 kJ/mol only. Besides, 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 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.[13,14,26]

Sample preparation

About 0.9 g of PVC was dissolved into 60 mL of THF and stirred using a magnetic stirrer until all PVC was dissolved completely. About 3.5 g of LENR50 which contains 2.1 g of DRC was poured into the solution and stirred for 24 h to form a homogenous solution. Five percent of $LiClO_4$ was then added into the mixtures solution and continued to be stirred for another 24 h. The resulting 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 amounts of THF solvent dried off, the sample was further dried in a vacuum oven at 50°C and 0.2 atm for 24 h to further remove the residue and solvent. The dried film was obtained after THF solvent has completely evaporated. The film was then peeled off from the dish. These steps were repeated for preparing PVC–LENR50 (30/70)–$LiClO_4$ with 10–40 wt % $LiClO_4$. This process will produce a mechanically stable and a free standing electrolytes film.

Sample characterization

The ionic conductivity measurement was performed by alternate current (AC) impedance spectroscopy using high-frequency response analyzer (HFRA Solartron 1256, Schlumberger) in the frequency range of 0.1 Hz to 1 MHz. The electrolyte films were sandwiched between two stainless steel electrodes with a surface contact area of 2.0 cm^2 and mounted onto the holder. From the Cole–cole plots obtained, the bulks resistance, R_b (Ω), of the samples was determined with Z-View software. The conductivity was calculated based on the equation $\sigma = l/R_b A$, where l is the film thickness (cm) and A (cm^2) is the effective contact area of electrolyte and the electrode. X-ray diffraction technique was conducted by Siemens model D5000 at room temperature to determine the crystalline phase of the polymer electrolyte samples. The X-ray source used was CuKα with wavelength of 1.5418 Å and diffraction angle, 2θ,
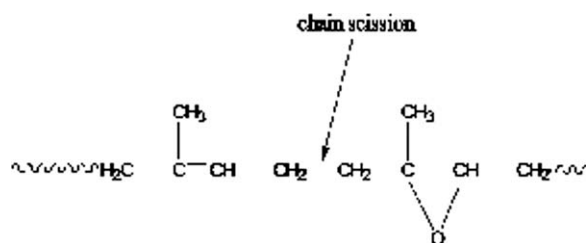
Figure 1 Degradation of ENR50 upon irradiation with UV light.
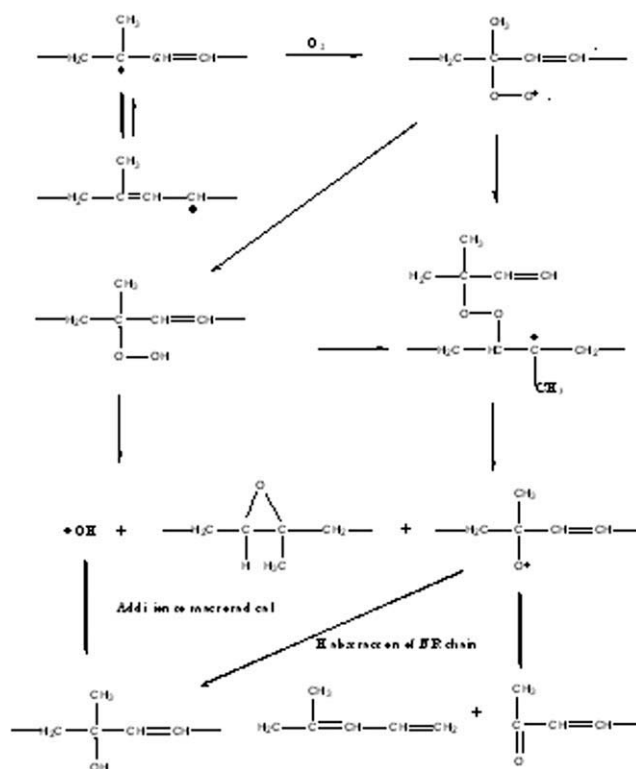
Figure 2 Structure and mechanism routes for irradiation of LENR50.

ranges from 2° to 60°. Thermal analysis was performed on the SPEs using differential scanning calorimeter (DSC) model Mettler Toledo 822. The SPEs samples were heated in range of –60 to 120 °C under nitrogen gas with heating rate of 10°C/min interval. The T_g of the samples which is at mid-point of the endothermic peak was evaluated from the STARe software. The morphological studies on the fractured surfaces of polymer electrolyte samples were done using SEM with 2000× magnification at 25 kV electron beam.
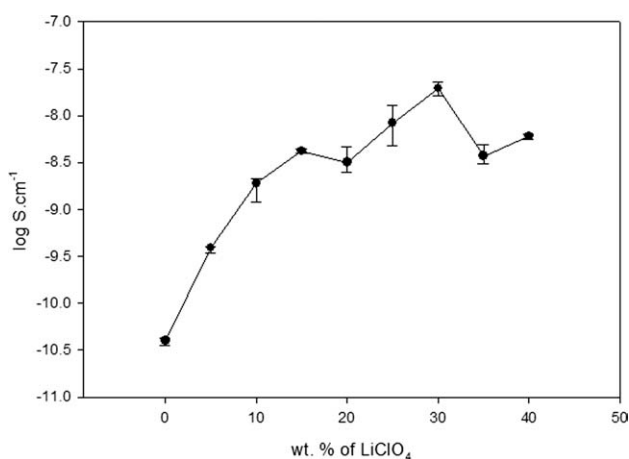
RESULTS AND DISCUSSION

Ionic conductivity

Table I and Figure 3 show the relationship between the bulk resistance and conductivity of PVC–LENR50–$LiClO_4$ electrolyte, respectively, with $LiClO_4$ salt concentration at room temperature. It can be seen that the ionic conductivity varies with the concentration of $LiClO_4$ salt. The ionic conductivity was increased from 0 to 30% of $LiClO_4$. However, further addition of $LiClO_4$ salt caused the ionic conductivity to drop. The highest ionic conductivity obtained was 2.3×10^{-8} S cm^{-1} at 30 wt % $LiClO_4$, while the lowest was 4.2×10^{-11} S cm^{-1} at 0 wt % $LiClO_4$. The ionic conductivity was improved by 548 times after the salt was added. From Table I, the smallest value of bulk

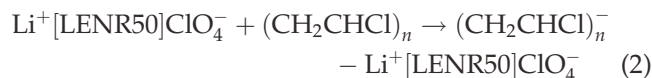| wt % LiClO$_4$ (g)	R_b (Ω)
0	1.9×10^8
5	2.3×10^7
10	5.5×10^6
15	3.0×10^6
20	2.7×10^6
25	1.1×10^6
30	7.0×10^5
35	3.3×10^6
40	2.8×10^6

resistance was observed at 30 wt % LiClO$_4$ with 7.0 × 10^5 Ω. The bulk resistance which was described by an arch was interpreted from the stimulation line (semicircle) performed on the impedance spectra in which the slanted spike represents the high-frequency semicircular region. These were attributed to the solid polymer electrolytes resistance.[15,27] The increase in the ionic conductivity after introduction of LiClO$_4$ salt into the electrolytes system was due to the fact of increasing charge carriers in the system increase. This can be shown by the equation: σ = $ce(u_+ + u_-) = c\Lambda$ where σ is conductivity of electrolytes, Λ is molar conductivity, c is salt concentration, e is charge on an electron, and u_+ and u_- represent the ion mobility. As number of charges increases, the ionic conductivity also increases.[1,7]

Furthermore, the increase in ionic conductivity of the SPE was attributed by the large volume of ClO$_4^-$ which may elongate the pitch of PVC and LENR50 spiral structures and thus provide a bigger transfer space for Li$^+$ ions.[3] The LENR50 was thought to have played the role of a "plasticizer" to reduce the viscosity of the PVC chains and hence increasing 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.[6,15,22] However, it is noted that after the introduction of optimum concentration of LiClO$_4$ salt, the ionic conductivity decreased. This implies that ions association likely occurred in the electrolytes system. Ions association caused the number of free ions to decrease which leads to the lower ionic conductivity values. This can be explained by the fact that at extreme low salt concentrations, the salts exist in the form of isolated Li$^+$ and ClO$_4^-$ ions. When the concentration of salt increases, mutual interactions between ions are sufficiently strong to promote the formation of ion pairs, which are in equilibrium with the free ions: Li$^+$ + ClO$_4^-$ ⇋ [LiClO$_4$]^0. Since the ions pairs carry no charge, the conductivity per unit salt concentration will drop as observed in Figure 3. The formation of the PVC–LENR50 (30/70)–LiClO$_4$ complex is described as[1,3,7,27]

$$LiClO_4 + LENR50 \rightarrow Li^+[LENR50]ClO_4^- \quad (1)$$

$$Li^+[LENR50]ClO_4^- + (CH_2CHCl)_n \rightarrow (CH_2CHCl)_n^- - Li^+[LENR50]ClO_4^- \quad (2)$$

Another possible reason is the excessive salt which will also increase the transient crosslinking in the electrolytes and thus reducing its chain mobility. This is further proved by the results in DSC. Besides, Xuping et al. noted that when the content of salt increases, the amount of ClO$_4^-$ will also increase in the mean time too, which will occupy the space of PVC network structure and thus block the diffusion of lithium ions.[3]

X-ray diffraction analysis (XRD)

Figure 4 illustrates the XRD patterns of pure PVC, LiClO$_4$ salt, and PVC–LENR50 (30/70)-based

Figure 3 Variation of ionic conductivity of the electrolyte with LiClO$_4$ salt content.
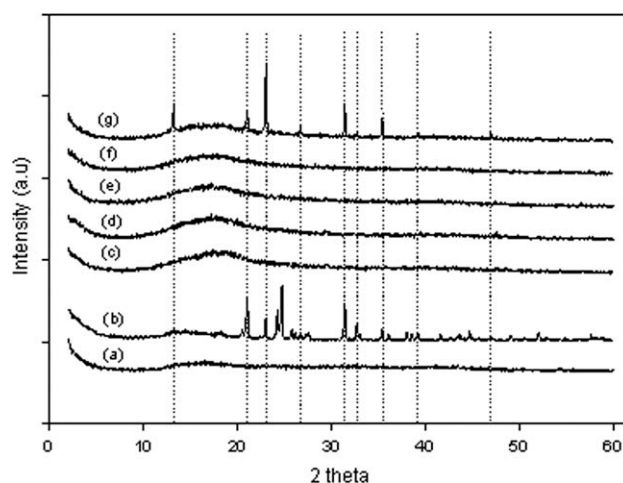
Figure 4 XRD patterns of (a) pure PVC, (b) LiClO$_4$, (c) 0 wt %, (d) 10 wt %, (e) 20 wt %, (f) 30 wt %, and (g) 40 wt % LiClO$_4$.

electrolytes system. The X-ray diffraction measurements were conducted in the range of 2°–60° to examine the nature of the crystallinity of the polymer–salt system complexes with respect to PVC–LENR50 (30/70) without salt and also to investigate the occurrence of complexation. There was no sharp peak observed for pure PVC except for a single broad peak. This implies that PVC is fully amorphous polymer. This broad peak is known as "amorphous hump" and is a typical characteristic of amorphous materials.[23]

Upon the addition of salt into the polymer host, there was no single sharp crystalline peak of lithium salt was observed for 10–30 wt % LiClO$_4$. The absence of crystalline peaks indicates that LiClO$_4$ is fully complexed with PVC–LENR50 (30/70) system. A complete dissolution of salts in polymer electrolytes leads to a complexation between PVC–LENR50 and LiClO$_4$ salt as complex process takes place in the amorphous region. This shows that ions prefer to dissolve in amorphous phase. In amorphous regions, greater ionic diffusivity can be produced as ions can move in the amorphous phase easily because of low energy barriers. Besides, the polymer that was amorphous exhibits more flexible backbone which can increase local chain mobility and hence increases the segmental motions of the polymer. Subsequently, this improved the transportation property of the electrolyte system. In addition, the segmental motions of the polymer chains in amorphous phase will promote ions motions by making and breaking the coordination sphere of the solvated ion and providing space (free volume) which the ions may diffuse under the influence of the electrical field.[28]

However, sharp peaks were observed when higher concentration of salt was added which was shown in Figure 4(g). Crystalline peaks were formed at angles of 13.2°, 21.0°, 23.0°, 26.6°, 31.4°, 32.8°, 35.5°, 39.2°, and 47.0°. At high concentration of LiClO$_4$ salt, recrystallization of LiClO$_4$ salt tends to occur from association of ions Li$^+$ and ClO$_4^-$ which can lead to decrease in ionic conductivity of SPEs. In other words, the optimum ionic conductivity value was found at 30 wt % LiClO$_4$ salt and ionic conductivity will drop after this value. As suggested by Wanchart et al., at salt higher than the solubility limit of the system, a crystalline complex is formed.[29]

Differential scanning calorimetry studies (DSC)

The DSC thermograms of the electrolytes are presented in Figure 5. DSC measurements were performed on the electrolytes to investigate the effect of the salt content on thermal property of the electrolyte. It was observed that the T_g increased with the addition of LiClO$_4$ salt content. The polymer electrolyte with 0 wt % LiClO$_4$ has T_g of 69.8°C and dra-
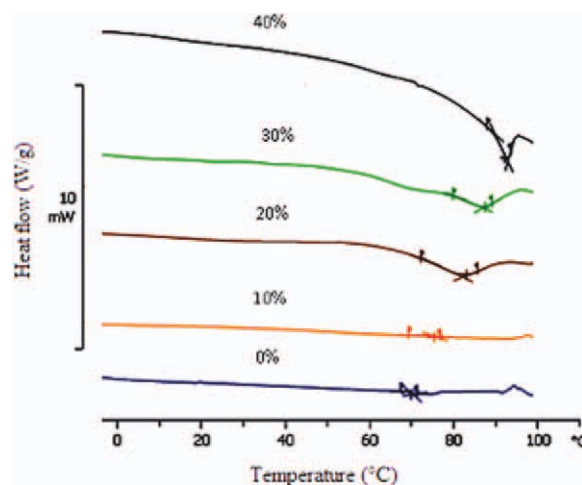

Figure 5 DSC thermograms of PVC–LENR50 (30/70) with different concentrations of LiClO$_4$ salt. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

matically increased to 88.3°C at 40 wt % LiClO$_4$. This shows that interaction occurred between LiClO$_4$ salt and PVC/LENR50 system. The shift to the higher T_g value due to the Li$^+$ ions prefer to interact with electron-rich coordinating groups, such as ether and carbonyl group, via transient crosslinkage bond.[30] These crosslinkage bonds obstruct the rotation of the polymer segments and hence increase the energy barrier to the segmental movement. Eventually, this cation–chlorine and cation–oxygen coordination bindings reduce the flexibility of polymer backbone.[23,30] Moreover, when the salt dissolves in polymer and dissociates to 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.[29] This phenomenon is due to salt ions acting as a transient crosslinking agent that increases the T_g and thereby decrease the ionic mobility. In addition, only one distinct peak was observed which indicates the homogenous behavior of the polymer electrolytes. Furthermore, it is known that additives such as Li$^+$, Fe^{2+}, Fe^{3+} ions are known to be active dechlorination agents for PVC and its derivatives. In some cases, anions such as ClO$_4^-$, I$^-$, and SO$_4^-$ can accelerate the thermal decomposition of PVC including drying process when solid polymer electrolyte is produced from solutions.[31] Eventually, dechlorination can promote the crosslinking between the polymer segments that lead to increase in T_g when more salts were doped in the polymer electrolyte.[30]

Scanning electron microscopy (SEM)

The SEM micrograph micrographs shown in Figure 6 were taken from the cross-sectional area of pure
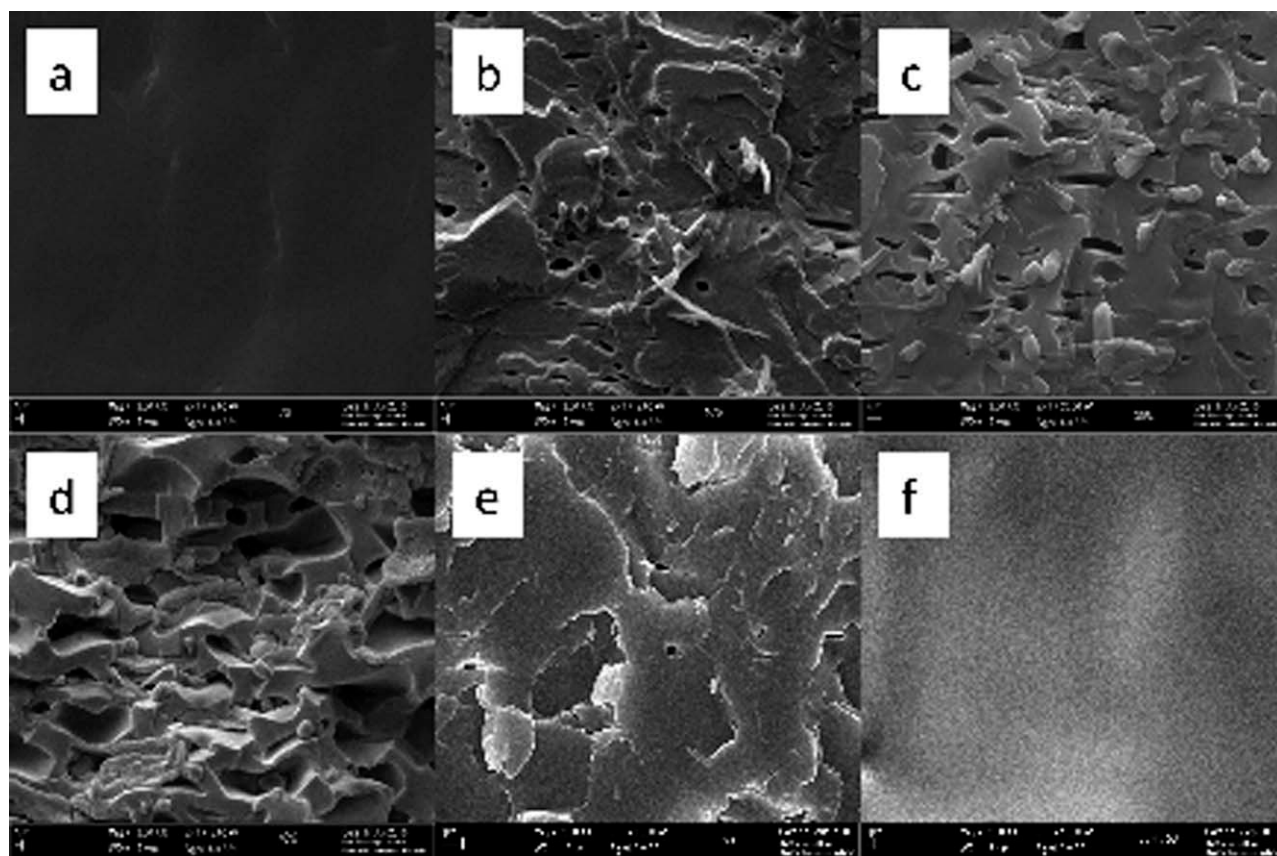
Figure 6 SEM micrograph of (a) SPE 0 wt %, (b) SPE 10 wt %, (c) SPE 30 wt %, (d) SPE 40 wt %, LiClO$_4$, (e) pure PVC, and (f) pure LENR50.

PVC, LENR50, and SPEs with different amount of LiClO$_4$ salts. In Figure 6(e), the cross section surface of PVC was relatively rough and with lots of cracks. Contrary to the inner surface of LENR50, the surface was smooth as shown in Figure 6(f). However, when the PVC and LENR50 were blended together, the surface of PVC was greatly improved as shown in Figure 6(a). There was no cracked surface and agglomerate observed. These concluded that PVC–LENR50 (30/70) blend was miscible and compatible. Moreover, the physical properties also improved as PVC and LENR50 compensate for each other's weaknesses with PVC improving the mechanical strength of LENR50 while LENR50 enhances the tear strength, adhesion, and elasticity of PVC. As a matter of fact, LENR50 has smaller molecular size that leads to larger interphasing area and higher interaction with PVC compared to ENR50.[13,32]

Figure 6(b–d) represents the cross section views of SPEs with 10, 30, and 40 wt % LiClO$_4$ salt, respectively. When the salt was added into the complexes system, the formation of micropores occurred. This phenomenon is due to the complex process of interaction between the solvent, lithium salt, and the polymers during evaporation.[7,30] In addition, it is also kinetically controlled by the relative rate of

evaporation of the compounds. Watchanida et al. explained that the porosity might be due to the repulsive forces between the carboxylic acid groups of the polymer host in which the carboxylic groups were formed from the OOH group.[33] In fact, the micropores in the polymer–salt matrix enhance the mobility of ions by providing and creating more pathways for ions transportation. However, Figure 3 shows that after 30 wt % salt, the conductivity dropped. This implies that the number of charge carriers decreased and ions association occurred as discussed in ionic conductivity section. Besides, the presence of higher lithium salt concentration can cause phase separation and agglomeration that hinder migration of Li$^+$ ions in the SPE, resulting in lower ionic conductivity. This was proven in Figure 6(d) as the surface of the cross-sectional area shows agglomerates.

CONCLUSIONS

Solid polymeric electrolyte of PVC–LENR50 (30/70) with function of LiClO$_4$ salt concentration was successfully prepared by solution casting technique. The highest ionic conductivity obtained is 2.3×10^{-8}

S cm^{-1} at 30 wt % LiClO$_4$ salt. Although PVC–LENR50 (30/70) blend was well miscible and compatible, it appeared that the ionic conductivities of the SPEs were still quite low at ambient temperature considering that the PVC–LENR50 (30/70) polymer host has high bulk resistance. This is because the PVC and LENR50 can form self-crosslinkable blends. It was proposed that PVC was the main contribution to the high bulk resistance outcomes because the excessive PVC adulteration increased the dehydrochlorination process, thus promoting the crosslinking between the polymer segments. Subsequently, this leads to insufficient flexibility of polymer chain and impedes the ion transportation. The XRD results further proved that 30 wt % salt was the optimum value as crystallization tends to occur on exceeding this value. In thermal studies, the T_g increased when the salt content increased because more crosslinkages were produced via coordination bonds between cations and polymers. The SEM studies showed that PVC and LENR50 were well miscible and compatible as suggested by other researchers. The smooth surface can make ions move more freely in the polymer electrolytes.

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