

Preparation and Characterization of Solid Polymeric Electrolyte of Poly(vinyl) Chloride-Low-Molecular Weight LENR50 (70/30)-LiClO₄

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ABSTRACT: This work presents the preparation of a free standing electrolyte film containing poly(vinyl) chloride (PVC) and 50% liquid epoxidized natural rubber (LENR50) blends as a host for the electrolyte that was doped with lithium perchlorate (LiClO₄) as the dopant salt. The electrolyte was prepared via solution-casting technique. From the impedance result, the highest ionic conductivity obtained was $9.6 \times 10^{-9} \text{ S cm}^{-1}$ at the 30 wt % of LiClO₄. This ionic conductivity result was supported by XRD analysis that showed the addition of 5–30 wt % of LiClO₄ salt to the PVC-LENR50 was well dissociated in the electrolyte as no salt peaks were observed. This implies that the salt was fully complexed in the system.

Thermal analysis revealed that T_g increased with lithium salts concentration. This is due to the formation of transient crosslinkage bonds and increasing viscosity. The morphological studies revealed the good homogeneity of the PVC-LENR50 (70/30) blend as no phase separation was observed. In addition, the formation of micropores with an addition of salts in the electrolyte improved the mobility properties of Li⁺ ions in the electrolyte system. Hence, it improves the ionic conductivity. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: PVC; LENR50; LiClO₄; ionic conductivity; polymer electrolyte

INTRODUCTION

Solid polymer electrolytes (SPEs) are considered to be the newest class of solid ionics and is currently receiving a great deal of attentions due to their proposed large-scale use in secondary lithium ion batteries and electro-chromic smart windows. Unlike the inorganic glass or ceramic electrolytes, the polymer electrolytes are compliant, and this property makes it possible to construct solid-state batteries in which polymer can well conform to the volume changes of the electrodes that typically occur during discharge and charging cycles. In comparison between SPE with the conventional liquid electrolyte, SPE offers many advantages and benefits such as solid-state noncorrosive medium, high-automation potential for electrode preparation and cell as well as assembly techniques, broad operating tem-

perature range, no separator, no filling procedure, and intrinsic safety. Moreover, SPE makes the fabrication of safe batteries possible and permits the development of thin batteries with flexible design.^{1,2}

Although the conventional poly(ethylene oxide)-based polymer electrolyte is the most extensively studied, several types of polymers such as poly(methyl methacrylate), poly(vinyl)chloride, poly(vinylidene) fluoride, and poly(vinyl) alcohol as well as poly(acrylonitrile) have been studied to see their potential as a polymer-based electrolyte. There are also numerous studies on various types of SPEs having different kind of combinations of polymer blends and salts. To act as a successful polymer host, a polymer or active part of a copolymer should generally have a minimum of three essential characteristics: (1) atoms or groups atoms with strong electron donor center to form coordinate bonds with cations; (2) low barriers to bond rotation in order for segmental motion of the polymer chain to readily take place; (3) a suitable distance between coordination centers, because the formation of multiple intrapolymer ion bonds appears to be important.²

There were several methods of improving the ionic conductivity of the SPE such as by adding

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inorganic compound fillers (ZnO, Al₂O₃, TiO₂, NiO, etc.), irradiate electrolytes with gamma irradiation, and the addition of plasticizers (EC and PC).^{3–5} Alternatively, polymer blending offers another useful technique to design polymer electrolytes with a wide variety of properties that can improve the ionic conductivity.⁶ From a wide range of polymer blends, those containing PVC is among the most important from both scientific and commercial points of view. This is due to the facts that PVC has lone pair electrons at the chlorine atom where inorganic salts can be solvated and also the dipole–dipole interaction between the hydrogen and chlorine atoms that can stiffen the polymer backbone.⁷ Commercially, PVC is inexpensive and it is compatible with large amount of plasticizers and while preserves good mechanical strength after blends.^{8,9} Earlier reports found that polymer blends consisted of PVC and epoxidized natural rubber (ENR) were miscible at any blend ratios. In addition, this modified natural rubber also possessed characteristics of low-glass transition temperature, soft elastomeric characteristic at room temperature, good elasticity, and adhesion that can provide better surface interaction between electrolyte and electrode.^{10,11}

Moreover, it is reported that PVC and ENR50 mixtures can be made more miscible by reducing the molecular weight of one or both components. This finding is based on the Flory–Huggins theory that enthalpy gained on mixing polymers is inversely related to their molecular number. Hence, in this research, we had further modified the ENR50 by reducing the molecular weight using the photochemical technique to produce LENR50. The lower molecular weight of modified epoxidized rubber is expected to aid better property modifications than the higher molecular mass rubber. This is because the rubber with lower chain length provides greater penetration onto PVC interstices enabling better solubilization of the PVC segments.¹² In this work, we report a new polymer electrolyte of PVC/LENR50 blends as polymer host that were doped with various wt % of LiClO₄ salt using solution casting technique to obtain free-standing film. Samples were characterized by impedance spectroscopy (EIS), X-ray diffraction (XRD), differential scanning calorimetry (DSC), and scanning electron microscope (SEM).

EXPERIMENTAL

Materials

PVC (Aldrich) with average molecular weight of 97,000 and ENR50 (Guthrie (M) Bhd.) was used in this work. Lithium perchlorate (LiClO₄, purity > 95%) was obtained from Aldrich Chemical Co. Tetrahydrofuran (THF) was purchased from JT Barker, and toluene was from R&M Chemical England.

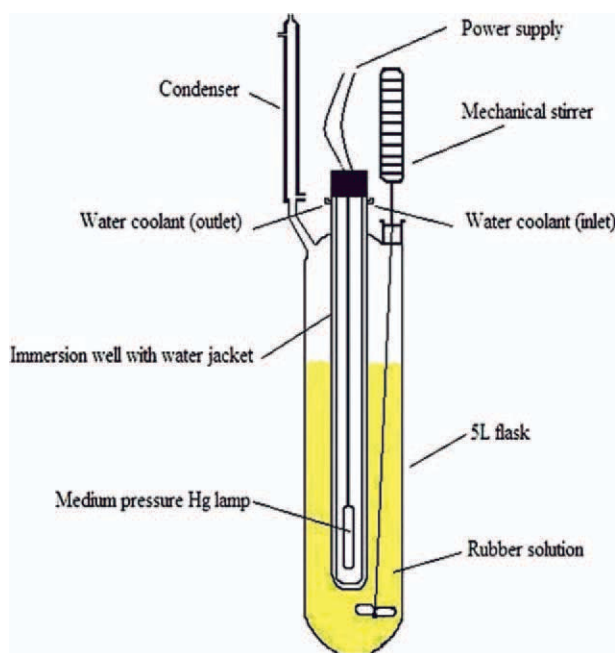


Figure 1 UV irradiation system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Sample preparation of LENR50

Before the rubber solution of 5 wt % was prepared, 250 g of 50 % ENR50 was cut into smaller size and put into 5 L of straight-sided cylindrical flask that contained 4750 g of toluene solvent. The cylindrical flask was fitted together with an immersion well, a stirring assembly, and a condenser as shown in Figure 1. 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 that 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 The mechanism of the depolymerisation of ENR50 to low-molecular weight LENR50 can be understood from Lee and coworkers and Dahlan et al.'s previous works.^{14,15} The molecular structure of ENR is shown in the reference by Rahman et al.¹⁴

Sample preparation of SPE

About 2.1 g of PVC was dissolved into 60 mL of THF and stirred using a magnetic stirrer until all PVC was dissolved completely. About 1.5 g of LENR50 that contains 0.9 g of DRC was poured into

the solution and stirred for 24 h to form a homogeneous solution. The 5 wt % LiClO₄ was then added into the mixture solution and continued to be stirred for another 24 h before being cast into a finely cleaned petri dish. It was then allowed to evaporate slowly in a fume hood at room temperature for a day. After an 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. The dried film was obtained after all the THF solvent has completely evaporated. The film was then peeled off from the dish. These steps were repeated to prepare PVC-LENR50 (70/30)-LiClO₄ with 10, 15, 20, 25, 30, 35, and 40 wt % of LiClO₄. This process produced a mechanically stable and a free standing electrolytes film with thickness range from 0.14 to 0.35 mm.¹⁶

Sample characterization

The ionic conductivity measurement was performed by alternate current (AC) EIS 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 cm² and mounted onto the holder. From the cole-cole plots obtained, the bulk 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 (cm²) is the effective contact area of electrolyte and the electrode. XRD 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 Cu K α with wavelength of 1.5418 Å and diffraction angle, 2θ range from 2° to 60°. Thermal analysis was performed using differential scanning calorimeter (DSC) model Mettler Toledo 822. The samples were heated in the range of -60–120°C under nitrogen gas with heating rate of 10°C/min interval. T_g of the samples, which is mid-point of the endothermic reaction, was evaluated from the STARE software.

TABLE I
Bulk resistance, R_b , of PVC-LENR50 (70/30) as a Function of LiClO₄ Salt Content

LiClO ₄ (wt %)	R_b (Ω)
0	4.6×10^8
5	1.4×10^8
10	1.8×10^7
15	1.2×10^7
20	2.6×10^7
25	9.9×10^6
30	1.7×10^6
35	6.4×10^6
40	2.3×10^7

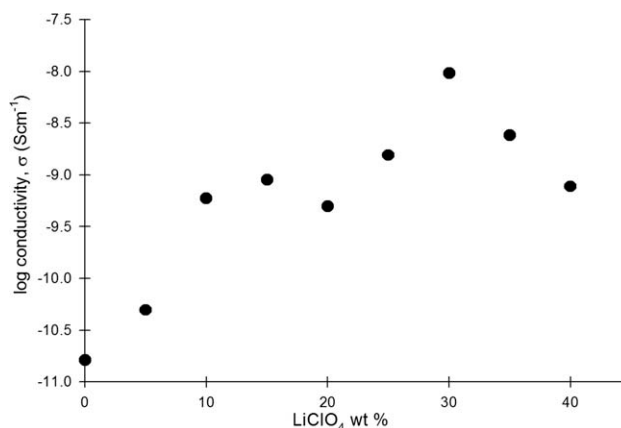


Figure 2 Ionic conductivity of PVC-LENR50 (70/30) doped with LiClO₄ salt.

The morphological studies on the fractured surfaces of polymer electrolyte samples were done using SEM with 2000 \times magnification at 25 kV electron beam.

RESULTS AND DISCUSSION

Ionic conductivity

Table I shows the relationship between the bulk resistance of the SPEs with different concentrations of LiClO₄ salt at room temperature. The plot of ionic conductivity versus concentration of lithium salts and typical cole-cole plot is shown in Figures 2 and 3, respectively. It was observed that the bulk resistance varies with the concentration of LiClO₄ salt.

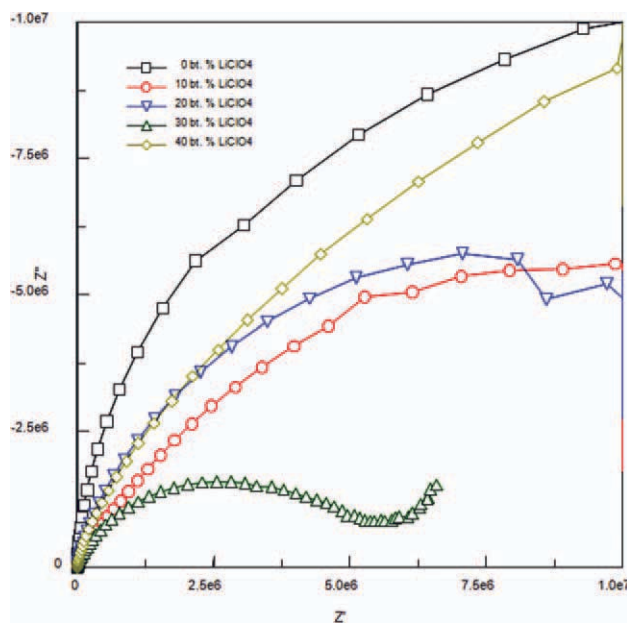
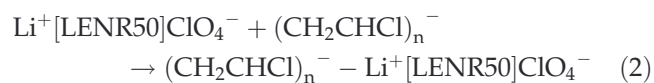


Figure 3 The typical cole-cole plot for PVC-low-molecular weight LENR50 (70/30) doped with lithium salts. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

Generally, the resistance of SPEs decreases from 0 wt % LiClO₄ to 30 wt % LiClO₄ before it increases at 40 wt %. In Figure 2, the lowest ionic conductivity was 0 wt % LiClO₄ with the value of 1.6×10^{-11} S cm⁻¹, and the highest value of 9.6×10^{-9} S cm⁻¹ was obtained at 30 wt % LiClO₄. The ionic conductivity of the electrolyte has been improved by 600 times when the salt was introduced into the complex system. The increase in the ionic conductivity after introduction of LiClO₄ salt into the electrolyte system was due to the increase of charge carriers in the system. This can be shown by the equation: $\sigma = ce(u_+ + u_-) = c \nabla$, where σ is conductivity of electrolyte, ∇ is molar conductivity, c is salt concentration, e is charge on an electron, while u_+ and u_- represent the ion mobilities. As number of charges increases, the ionic conductivity also increases.^{1,16} Noor et al.¹⁷ reported that PEO/ENR50 (70/30) blend exhibits conductivity at 2.2×10^{-7} S cm⁻¹ compared to PVC/LENR50 (70/30) at 1.6×10^{-11} S cm⁻¹. It was proposed that PVC was the main contribution to the high-bulk resistance outcomes due to its properties explained earlier. The excessive PVC adulteration will increase 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.¹⁸ However, after the optimum value of 30 wt % LiClO₄ salt was introduced, the ionic conductivity started to decrease. This implies that ions association was likely to occur in the electrolytes system. Ion association causes the number of free ions to decrease that lead to the lower ionic conductivity values. This can be explained whereby at extreme low-salt concentrations, the salts exist in the form of isolated Li⁺ and ClO₄⁻ ions. As the concentration increases, mutual interactions between ions are sufficiently strong to promote the formation of ion pairs, which are in equilibrium with the free ions: $\text{Li}^+ + \text{ClO}_4^- \leftrightarrow [\text{LiClO}_4]^0$. Because the ion pairs carry no charge, the conductivity per unit salt concentration will drop as observed in Figure 2. The formation of the PVC-LENR50 (70/30)-LiClO₄ complex is described in Refs. 1,16–18:



X-ray diffraction

Figure 4 illustrates the X-ray diffraction (XRD) pattern of pure PVC, LiClO₄ salt, and the electrolytes in the range of 2°–60°. XRD analysis was performed to determine the structures as well as the degree of crystallization of the polymer-salt system complexes

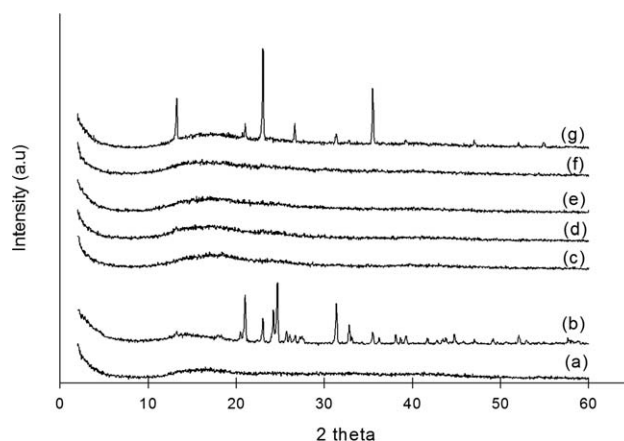


Figure 4 XRD patterns of (a) pure PVC, (b) LiClO₄, (c) 0, (d) 10, (e) 20, (f) 30, and (g) 40 wt % of LiClO₄.

by observing the appearance and disappearance of the crystalline phase. XRD patterns of the pure PVC and LiClO₄ salt are represented by Figure 4(a,b). For pure PVC, no sharp peak appeared except for a single broad peak that suggested that PVC is a fully amorphous polymer. This broad peak is known as the “amorphous hump” and is a typical characteristic of amorphous materials.¹⁹

Upon adding salts into the polymer electrolytes, no single sharp crystalline peak of lithium salt was observed for 10–30 wt % of LiClO₄. The absence of crystalline peak of the excess salt indicates that LiClO₄ is fully complexed with PVC and LENR50. A complete dissolution of salt in polymer electrolytes leads to a complexation between salt and polymer as complex process takes place in the amorphous region. The amorphous nature produces greater ionic diffusivity that leads to high-ionic conductivity. This can be achieved, because the amorphous polymer has a fully flexible backbone that can increase local chain mobility, resulting to the increase of segmental motion of the polymer. Hence, this improves the transportation property of the electrolyte as local chain mobility increased. In addition, the segmental motions of the polymer chains in amorphous phase are important to promote ion motion by making and breaking the coordination sphere of the solvated ion and providing space (free volume) into which the ion may diffuse under the influence of the electric field.¹

However, crystalline phase arose with the presence of LiClO₄ peaks formed at angles 13.24°, 21.0°, 23.0°, 26.64°, 31.36°, and 35.48° when incorporating at 40 wt % of LiClO₄ salt. This is because at high concentration of LiClO₄ salt, recrystallization of LiClO₄ salt tends to occur from association of ions Li⁺ and ClO₄⁻ that can lead to the decrease in ionic conductivity of SPE. In other words, the optimum ionic conductivity value was found at 30 wt % of LiClO₄ salt

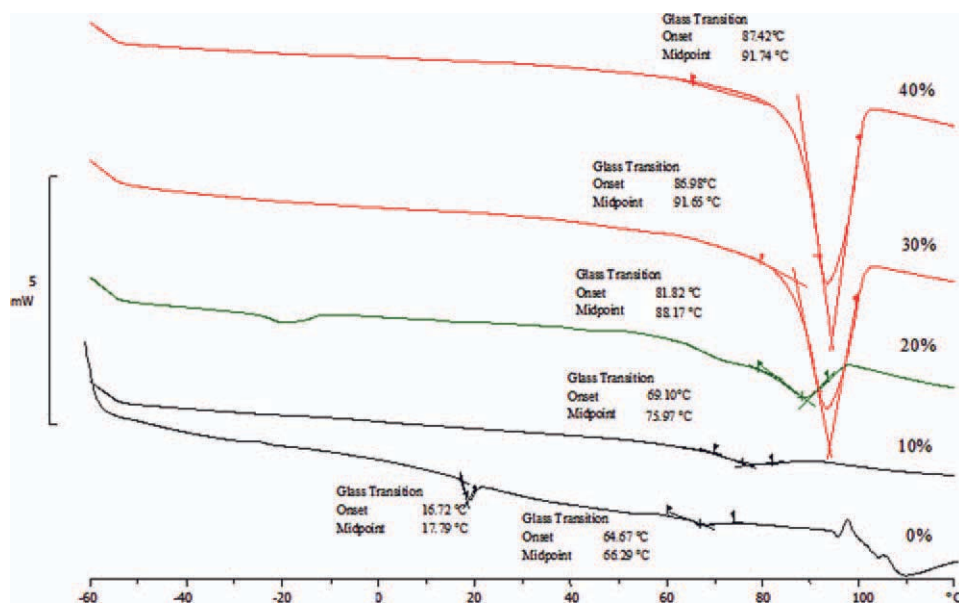


Figure 5 DSC thermograms of PVC-LENR50 (70/30) doped with various concentration of lithium salts. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

loading, and the ionic conductivity will drop after this value.

Differential scanning calorimetry studies

The differential scanning calorimetry (DSC) thermograms of SPEs are presented in Figure 5. DSC measurements were performed on SPEs to investigate the effect of the salt content on glass transition temperature of the electrolyte. It was observed that T_g and T_m increase with LiClO₄ salt content. The polymer electrolyte with 0% wt LiClO₄ demonstrates T_g at 17.8 and 66.3°C, whereas the electrolyte with 10% wt LiClO₄ shows T_g at 76.0°C. However, at 20% wt LiClO₄ and higher concentration of salt, sharper peaks of T_m were observed and dramatically increased from 88.2 to 91.7°C at 40% wt LiClO₄ indicating the formation of an eutectic between polymer host and the salt in which phase separation occurred after 30 wt % as proven in XRD.²⁰ This phenomenon also indicates that interaction occurs between LiClO₄ salt and PVC-LENR50 polymer host via formation of coordination bonds leads to the decrease in the disorder phase and hence promote crystalline phase. The shift to the higher T_g and T_m value is due to the Li⁺ ions preferring to interact with electron-rich coordinating groups, such as ether and carbonyl group via transient crosslinkage bond.¹⁸ These crosslinkage bonds cause obstruction to the rotation as well as mobility of the polymer segments and hence increase the energy barrier to the segmental movement. Eventually, this cation-chlorine and cation-oxygen co-ordination bindings reduce the flexibility of polymer backbone.^{18,19} Moreover, when salt dis-

solves 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.²¹ This is because the salt ions act 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. Besides, additives such as Li⁺, Fe²⁺, and Fe³⁺ ions are known to be active dechlorination agents for PVC and its derivatives. In some cases, anions such as ClO₄⁻, I⁻, and SO₄⁻ can accelerate the thermal decomposition of PVC including drying process when SPE is produced from solutions.¹⁷ Eventually, dechlorination can promote the crosslinking between the polymer segments that leads to increase in T_g and T_m when more salts was doped in the polymer host.¹⁸

SEM analysis

Scanning electron microscope (SEM) micrograph images were taken at the cross-sectional area of pure PVC, LENR50, and polymer electrolytes are shown in Figure 6(a-f). It can be seen that LENR50 has smooth and clean surface, whereas the surface morphology of pure PVC was rough and cracked. As expected, the brittleness and fracture surfaces of PVC were improved when LENR50 was blended together with PVC as shown in Figure 6(a). This showed that LENR50 forms miscible blend with PVC and enhances the tear strength of the PVC,

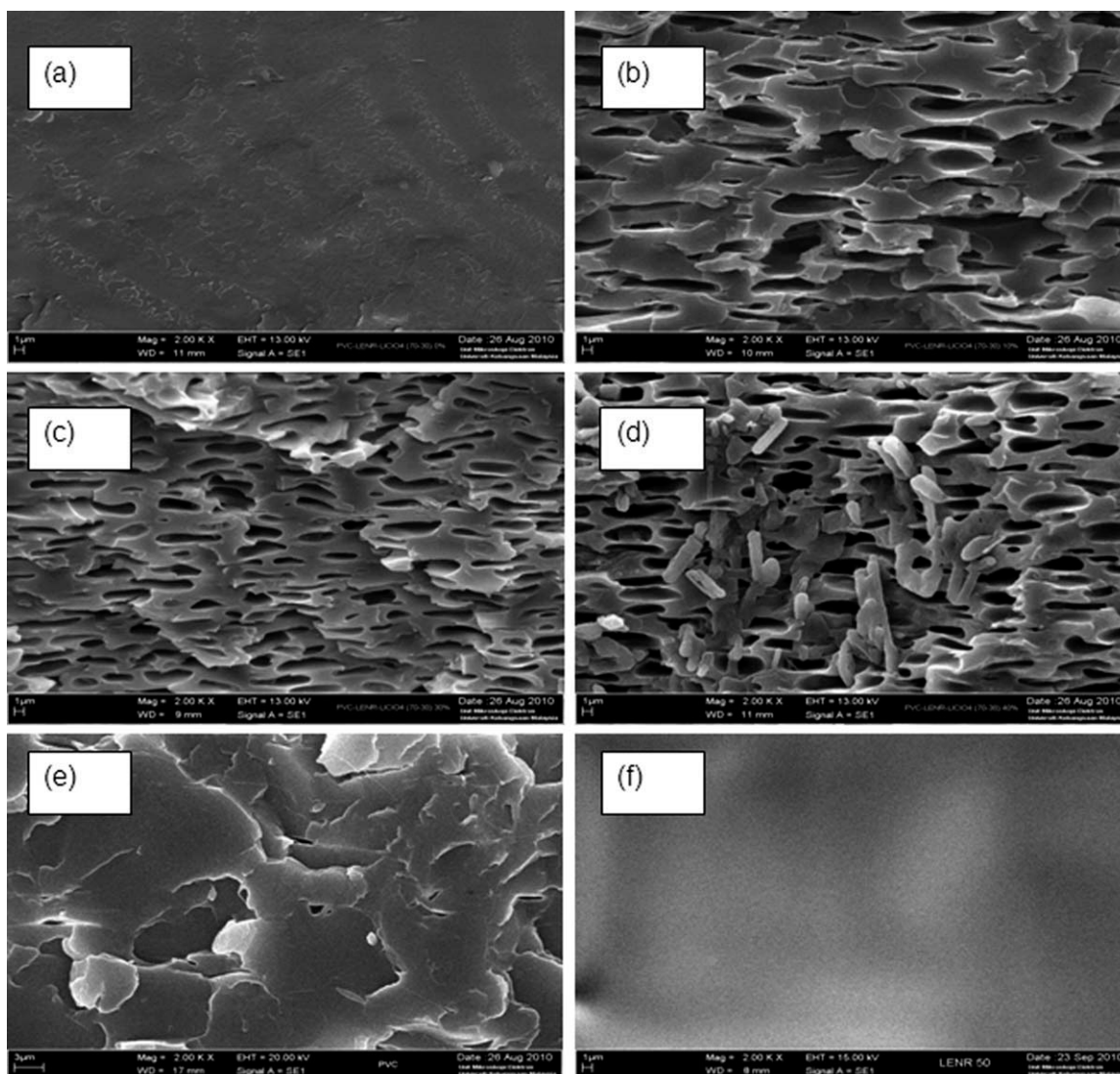


Figure 6 SEM image of (a) SPE 0 wt % salt, (b) SPE 10 wt % salt, (c) SPE 30 wt % salt, (d) SPE 40 wt % salt, (e) pure PVC, and (f) pure LENR50.

resulting better physical properties. In fact, LENR50 has better miscibility, higher interaction, and larger interphasing area with PVC owing to its smaller molecular size.^{11,14,15}

The fractured structural views of the samples in Figure 6(b–d) show the formation of micropores that occurred from the complex process of interaction between solvent and the polymers. Furthermore, it is also kinetically controlled by the relative rate of evaporation of the compounds.¹⁴ It is well known that the fine pores in the polymer matrix aid ion mobility by providing more alternative path ways for ions transportation. The micropores structures increased with higher concentration of lithium salt. These results and suggestions were further strengthened by results of ionic conductivity measurement that showed that the highest ionic conductivity value achieved at 30% wt LiClO₄ where the most micropores were formed. Figure 6(d) also showed

the occurrence of agglomerations and was supported by the presence of crystalline peaks in XRD analysis which was due to the association of ions after the optimum value. Hence, the value of ionic conductivity dropped after 30% wt salt as the number of charge carriers decreased. The presence of the excess lithium salts can cause phase separation and blockage that hinder migration of Li⁺ ions in the polymer, resulting lower ionic conductivity.¹⁸

CONCLUSIONS

Solid polymeric electrolyte of PVC-LENR50 (70/30) with LiClO₄ salt was successfully prepared by solution-casting technique. The results showed that ionic conductivity was affected by the concentration of the % wt LiClO₄ salt, and the highest ionic conductivity obtained was $9.6 \times 10^{-9} \text{ S cm}^{-1}$ at 30% wt LiClO₄ salt. Although PVC/LENR50 (70/30) blend was well

miscible and compatible, it appeared that the ionic conductivity of the SPEs was still quite low at ambient temperature considering that the PVC/LENR50 (70/30) polymer host has high-bulk resistance. One of the reasons for the high-bulk resistance is PVC, and LENR50 can form self-crosslinkable blends. Besides, the excessive PVC adulteration will also increase the dehydrochlorination process, thus contributing to the crosslinking between the polymer segments and decreasing the flexibility of polymer chains. In another word, ion transportation that depends on mobility of polymer chains was impeded. The XRD results further proved that 30% wt salt was the optimum value as crystallization tends to occur after exceeding this value. In thermal studies, the T_g increased when the salt content increased because of more crosslinkage were produced via coordination bonds between cations and polymers. The SEM studies showed that PVC and LENR50 were well miscible as suggested by other researchers.

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