

Morphological, Infrared, and Ionic Conductivity Studies of Poly(ethylene oxide)–49% Poly(methyl methacrylate) Grafted Natural Rubber–Lithium Perchlorate Salt Based Solid Polymer Electrolytes

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ABSTRACT: The potential of poly(ethylene oxide) (PEO) and 49% poly(methyl methacrylate) grafted natural rubber (MG49) as a polymer host in solid polymer electrolytes (SPE) was explored for electrochemical applications. PEO–MG49 SPEs with various weight percentages of lithium perchlorate salt (LiClO_4) was prepared with the solution casting technique. Characterization by scanning electron microscopy, Fourier transform infrared spectroscopy, and impedance spectroscopy was done to investigate the effect of LiClO_4 on the morphological properties, chemical interaction, and ionic conductivity behavior of PEO–MG49. Scanning electron microscopy analysis showed that the surface morphology of the sam-

ple underwent a change from rough to smooth with the addition of lithium salts. Infrared analysis showed that the interaction occurred in the polymer host between the oxygen atom from the ether group (C–O–C) and the Li^+ cation from doping salts. The ionic conductivity value increased with the addition of salts because of the increase in charge carrier up to the optimum value. The highest ionic conductivity obtained was 8.0×10^{-6} S/cm at 15 wt % LiClO_4 . © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4222–4229, 2012

Key words: charge transport; charge transfer; conducting polymers; electrochemistry

INTRODUCTION

Solid polymer electrolytes (SPEs) are formed from complexation between dissolved polymers with metal salts.¹ The study of polymer–salt complexes was first started by Fenton et al.² in 1973. They found out that a poly(ethylene oxide) (PEO) film with a metal salt was conducting in a solvent-free system. Conversely, the potential of polymer–salt complexes in electrochemical device applications were only realized after the discovery by Armand et al.³ in 1978. Polymer electrolytes offer more advantages in comparison to conventional liquid electrolytes in terms of their shape, mechanical strength, and contact between the electrode and electrolyte interfaces.⁴ In addition, solid electrolytes are safer than liquid electrolytes as they do not have a leakage problem and because of their nontoxic properties. However, the conductivity values of SPEs at room temperature ($\sim 10^{-4}$ to $\sim 10^{-3}$ S/cm) are still

too low to be applied widely. To do so, SPEs need to overcome such problems. Research on PEO as a polymer host in polymer electrolytes has been done widely elsewhere.^{5–9} However, PEO has multifaceted structural properties because of the presence of crystalline and amorphous phases in the polymer host. There are several approaches for reducing the crystallinity in the polymer host, including crosslinking, blending, and copolymerization.¹⁰ To enhance the conductivity value and electrochemical stability of the electrolyte, polymer blending has been introduced between PEO and modified rubber. We believe that after the blending procedure, the modified rubber will promote a more amorphous phase in PEO. This will improve the segmental motion of the polymer chain and contribute to an increase in the ionic mobility and, thus, enhance the ionic conductivity.

Rubber-based polymer electrolytes have drawn the attention of many researchers.^{11–17} Modified natural rubber has attractive attributes; such as its free standing, flexibility, and good elasticity. A suitable elasticity can result in a flat and flexible film. Therefore, excellent contact is expected between an electrolytic layer and an electrode in a battery system.

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Modified natural rubber with polar groups can also act as a polymeric solvent, and the ionic conductivity value is expected to be higher in comparison to that of the glassy or crystalline state of the polymer.⁵ Examples of modified natural rubber are epoxidized natural rubber and poly(methyl methacrylate) grafted natural rubber (MG); they have oxygen atoms with a lone pair of electrons, which act as electron-donor atoms in the structure of the polymer host. However, the epoxidized natural rubber film shows drawbacks with regard to its mechanical properties, such as a slight stickiness and difficulty in peeling it off a substrate, in comparison to MG films.^{11,12,18} MG film as an electrolytes film has been potentially proven to have an acceptable conductivity value, is free standing and flexible, and has good elasticity. MG also has oxygen atoms contributed by methyl methacrylate (MMA) monomer that has been grafted to the polyisoprene chain. The interaction between the oxygen atoms with lithium ions from the metal salt form a coordinate bond; this results in the formation of polymer-salt complexes.^{13,14} Previous studies on various MGs have been conducted by others.^{13,15,16}

In this work, a PEO-49% poly(methyl methacrylate) grafted natural rubber (MG49) polymer blend (60:40 w/w) was doped with lithium perchlorate salt (LiClO_4) to prepare SPEs by a solution casting technique. All of the samples were characterized with alternating-current electrochemical impedance spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM). It was expected that LiClO_4 would raise the conductivity value in the PEO-MG49 system.

EXPERIMENTAL

Materials

PEO, with a weight-average molecular weight of 6000, was purchased from Sigma-Aldrich (St. Louis, MO). MG49 was commercially obtained from Green HPSP (Malaysia) Sendirian Berhad (Sdn. Bhd.), and LiClO_4 salts were supplied by Fluka/Sigma Aldrich, St. Louis, MO. The organic solvent tetrahydrofuran (THF) was supplied by System ChemAR, Kielce, Poland. All of the materials were used without further purification.

Sample preparation

Samples were prepared by a solution casting technique. A quantity of 2.1 g of MG49 was dissolved in stoppered flasks containing 45 mL of THF. After 24 h, the solution was stirred with efficient magnetic stirring for the next 24 h until complete dissolution of MG49 was achieved. PEO solution (0.9 g) was

prepared in another stoppered flask containing 30 mL of THF and stirred with continuous heating at 55°C for 24 h. These two solutions were then mixed together for 24 h to obtain a homogeneous solution. LiClO_4 salt at different weight percentage was dissolved in THF solution for 1 h and added to the solutions for the next 12 h with continuous stirring. PEO-MG49 polymer electrolyte solution (20 mL) was then cast onto a glass Petri dish to obtain a consistent thickness of the film in the range 0.01 ± 0.005 cm. The electrolyte solutions were cast onto glass Petri dishes, and the solvent was allowed to slowly evaporate in a fume hood at room temperature. Residual solvents were then removed in a vacuum oven for 24 h at 60°C. The samples were then stored in a desiccator until further usage. The same experiment procedure was repeated for different weight percentages of salt from 5 to 25 wt %.

Characterization

Physical observations were carried out with a Sony digital single lens reflex camera model $\alpha 350$. The surface morphology of the sample was observed with SEM (Philips XL30) with 1000 \times magnification and a 20-kV electron beam. The sample was fractured in liquid nitrogen and sputter-coated with gold before the analysis. FTIR spectra were recorded by a computer-interfaced PerkinElmer Paragon 500 spectrometer. The electrolyte was placed onto NaCl windows and analyzed in the frequency range between 4000 and 400 cm^{-1} with a scan resolution of 4 cm^{-1} . The ionic conductivity measurements were carried out by electrochemical impedance spectroscopy with a high-frequency resonance analyzer model 1255 with an applied frequency from 1 MHz to 0.1 Hz provided by Schlumberger, Paris, France. The disc-shaped sample 16 mm in diameter was sandwiched between two stainless steel block electrodes. All of the analysis was done at room temperature.

RESULTS AND DISCUSSION

Physical and morphological observation

Figure 1 shows the physical observation of PEO-MG49 at different weight ratios: 80 : 20 [Fig. 1(a)], 60 : 40 [Fig. 1(b)], 40 : 60 [Fig. 1(c)], and 20 : 80 [Fig. 1(d)]. Well-separated phases were observed between PEO and MG49, as shown in Figure 1(a,c). Meanwhile, Figure 1(d) shows bad mixing and poor physical properties in PEO-MG49 with a 20 : 80 ratio. PEO-MG49 at a 60 : 40 ratio, in Figure 1(b), had a more homogeneous surface and was free-standing, flat, and flexible with a suitable elasticity. Therefore, PEO-MG49 at a 60 : 40 ratio was chosen to continue with the addition of different weight percentages of salt from 5 to 25 wt %. Figure 2 shows the SEM

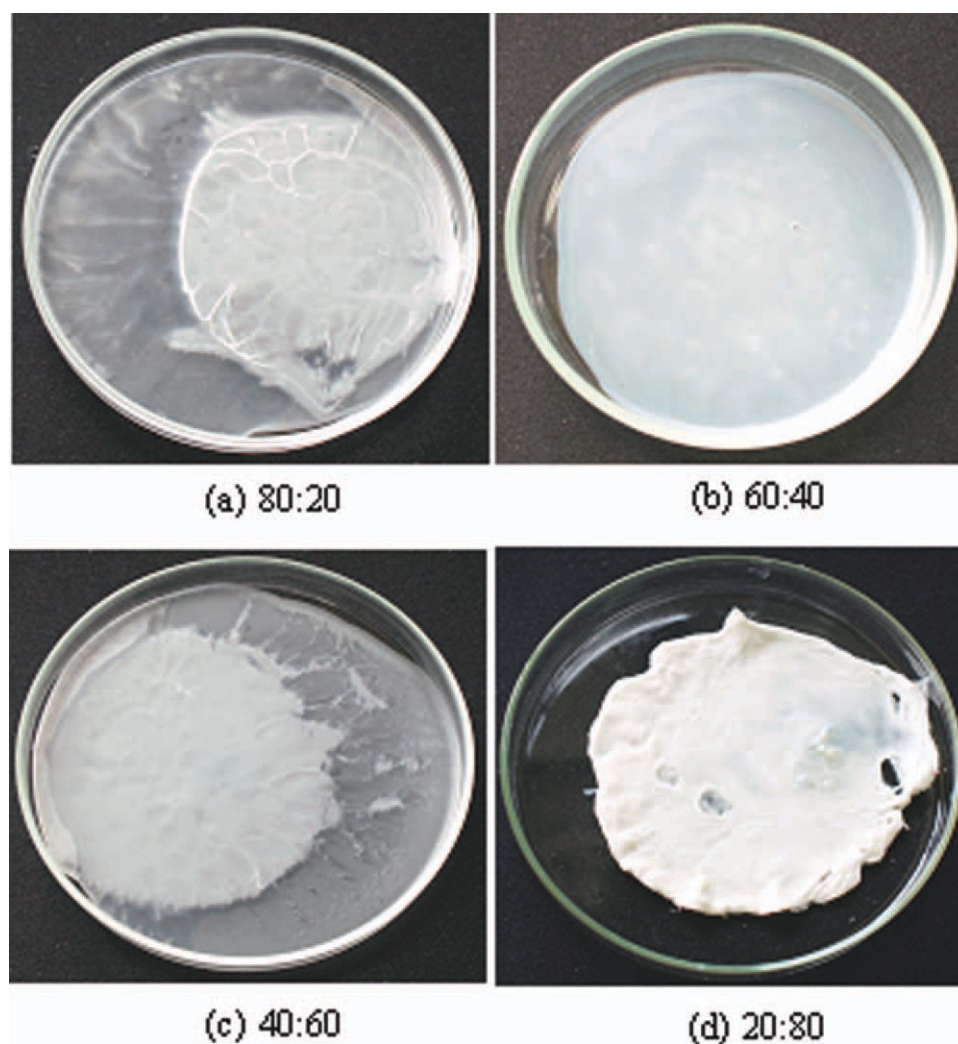


Figure 1 Physical observation of PEO–MG49 at different weight ratios: (a) 80 : 20, (b) 60 : 40, (c) 40 : 60, and (d) 20 : 80.

micrographs of pure MG49 [Fig. 2(a)], pure PEO [Fig. 2(b)], PEO–MG49 at a 60 : 40 ratio [Fig. 2(c)], PEO–MG49–10 wt % LiClO₄ [Fig. 2(d)], PEO–MG49–15 wt % LiClO₄ [Fig. 2(e)], and PEO–MG49–25 wt % LiClO₄ [Fig. 2(f)]. The SEM micrograph in Figure 2(a) shows the smooth and homogeneous surface of modified natural rubber, MG49, which was due to the amorphous nature of natural rubber. Meanwhile, Figure 2(b) indicates that PEO had a rough surface morphology with the presence of rumples. This figure shows the presence of a crystalline phase in PEO.⁶ When the MG49 was blended with PEO, the surface morphology of PEO changed from rough to a uniform and homogeneous texture during the rubber phase. PEO was well distributed in the rubber phases because it could be observed on the rubber texture. After 10 wt % LiClO₄ salt was added, the ruffled surface disappeared, and a co-continuous morphology was observed. The co-continuous morphology became smoother at 15 wt %, the optimum conductivity of

PEO–MG49–LiClO₄. The smooth surface indicated that the salt was dissolved in the polymer matrix. The dissociation of salt caused the interaction between salt and the polymer host.¹⁹ Additionally, the cross-sectional view of the sample in Figure 2(d–f) shows the formation of micropores due to the interaction between the solvent and the polymer host.²⁰ It was observed that the size of micropores, in Figure 2(d), increased with the addition of LiClO₄ salt. According to Ahmad et al.,²¹ the presence of pores will give a compensating effect on the transporting properties of Li⁺ ions by increasing the surface area. Hence, it improves the conductivity of the electrolytes. The SEM micrograph in Figure 2(f) also shows an increase of pores size and rough surface on the polymer host.

Infrared analysis

An infrared technique was used to examine the presence of polar functional groups, and interaction

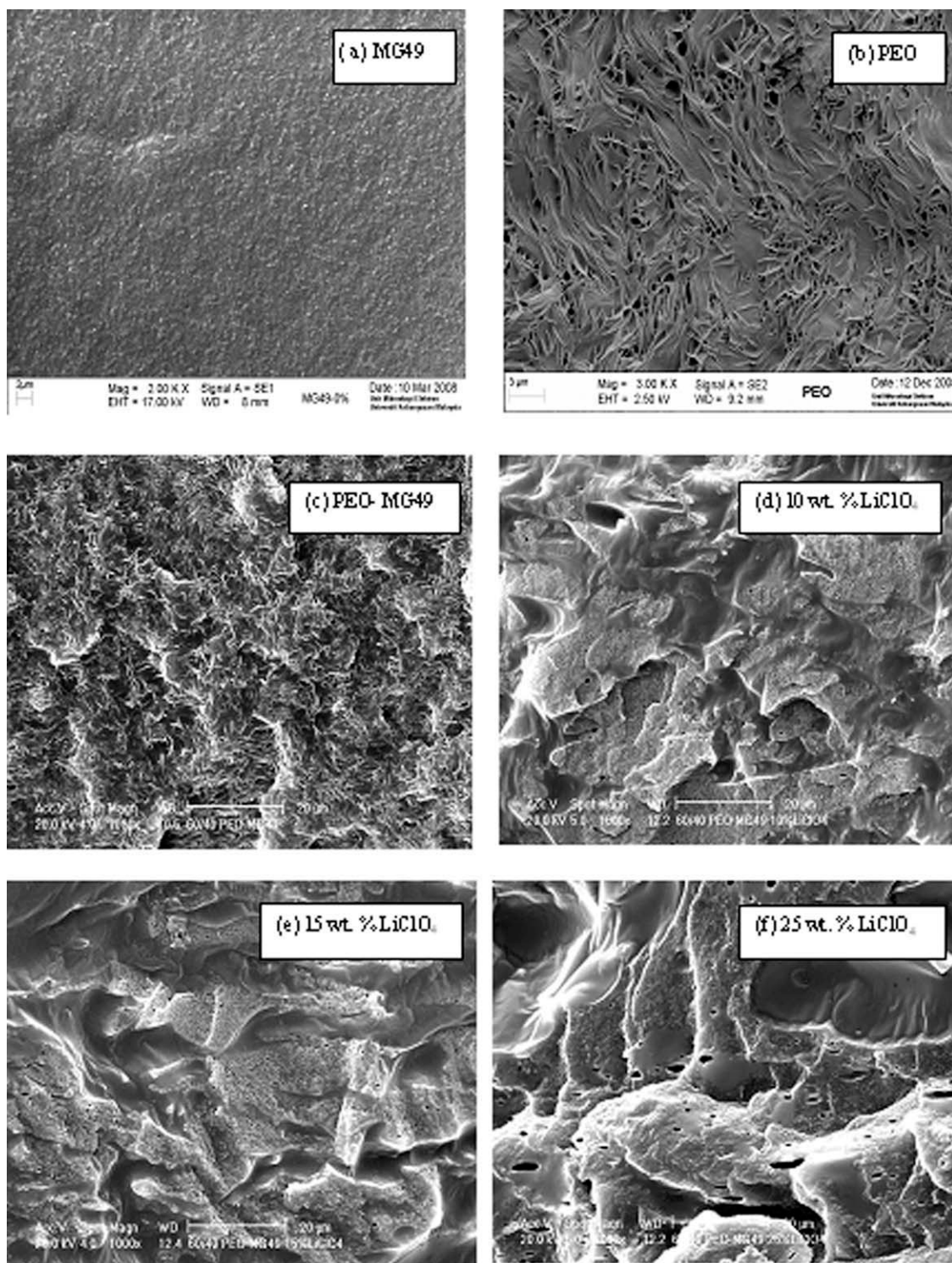


Figure 2 SEM micrographs of (a) pure MG49, (b) pure PEO, (c) PEO-MG49 at a 60 : 40 ratio, (d) PEO-MG49-10 wt % LiClO_4 , (e) PEO-MG49-15 wt % LiClO_4 , and (f) PEO-MG49-25 wt % LiClO_4 .

occurred in the systems. The main concerns were the polar groups on the polymer chain, such as ether groups ($\text{C}-\text{O}-\text{C}$, $1300\text{--}1000\text{ cm}^{-1}$) and carbonyl groups ($\text{C}=\text{O}$, $1750\text{--}1730\text{ cm}^{-1}$). According to the literature, the oxygen atoms in the structure of the polymer host act as electron-donor atoms and form

a coordinate/dative bond with lithium ions from doping salts to form a polymer-salt.^{13-16,22} The vibration frequency of the polymer-salt complexes will then be shifted to lower wavenumbers by about $15\text{--}25\text{ cm}^{-1}$ in comparison to the pure polymer host.²³ Table I shows the vibration frequency of each

TABLE I
Wavenumbers (cm^{-1}) of the Specific Vibration Modes of PEO-MG49-LiClO₄

Sample (wt % LiClO ₄)	ν (C=O)	ν (LiClO ₄)	ν (ClO ₄ ⁻)	ν_{as} (C—O—C)	δ (O—CH ₃)	ν (CH ₂) rocking	ν (CH ₂) twisting	ν (CH ₂) wagging
0	1728	1634 ^a	674, ^a 614 ^a	1146, 1099, 1060, 1095 ^a	1466	961, 841	1278, 1240	1359, 1342
5	1729	1648	622	1145, 1093, 1056	1466	958, 841	1279, 1240	1341
10	1728	1645	623	1094	1450	959, 842	1278, 1242	1342
15	1729	1644	622	1069	1451	947, 840	1245	1347
20	1728	1646	622	1070	1448	949, 838	1247	1350
25	1728	1643	622	1066	1450	949, 838	1247	1351

^a Pure LiClO₄.

bonding occurring in PEO-MG49-LiClO₄. Meanwhile, Figure 3(a,b) shows the FTIR spectra of the carbonyl and ether functional groups of PEO-MG49-LiClO₄.

Figure 3(a) shows the FTIR spectrum of the symmetrical stretching of carbonyl groups, $\nu(\text{C}=\text{O})$, from the MMA structure in MG49. The $\nu(\text{C}=\text{O})$ frequency of MMA gave rise to an intense, very strong, and sharp peak at 1728 cm^{-1} . The intensity of $\nu(\text{C}=\text{O})$ of the MMA peak was suddenly reduced upon the addition of 5 wt % LiClO₄ salts and increased together with the addition of the lithium salt system to 25 wt %. However, the shifting in wavenumbers was not significant enough to prove the interaction that occurred at the carbonyl group because the resolution was only within 4 cm^{-1} . Eventually, the FTIR spectra in Figure 3(a) showed the shifting of LiClO₄ peaks at 1648 and 622 cm^{-1} after the introduction of 5 wt % LiClO₄ salts, as compared to the pure LiClO₄ peaks at 1634, 674, and 614 cm^{-1} . Ali et al.²⁴ reported that the peak of SO₃ symmetric stretching from the triflate anion originated from lithium triflate salt shifting to lower wavenumbers in polymer-metal complexes. The peak shift indicated that an interaction occurred in the polymer-metal complexes. The specific vibration mode of ether groups (C—O—C) in PEO-MG49 was observed in the stretching mode of the C—O—C triplet peak in PEO, $\nu_{\text{s}}(\text{C}—\text{O}—\text{C})$, at 1146, 1099, and 1060 cm^{-1} , and the O—CH₃ asymmetric deformation mode of MMA in MG49 was observed at $\delta(\text{O}—\text{CH}_3)$ at 1466 cm^{-1} . The semicrystalline phase of PEO was confirmed by the presence of the triplet peak of C—O—C stretching.^{19,25} With the addition of LiClO₄ salt, the stretching mode of the C—O—C triplet peak, $\nu_{\text{s}}(\text{C}—\text{O}—\text{C})$, changed to a singular peak at 1066 cm^{-1} , and the O—CH₃ asymmetric deformation mode of MMA, $\delta(\text{O}—\text{CH}_3)$, was shifted to a lower wave number, 1450 cm^{-1} . This observation showed that the C—O—C band was strongly affected by the cation complexation. Additionally, the reduction and broadening of intensity could be clearly observed, as shown in Figure 3(b). The peak shift confirmed the interaction between lithium ions from the doping salt and oxygen atoms in the structure of the poly-

mer host. The reduction, broadening of intensity, and peak shift indicated that the remaining vibration frequency between C—O—C bonding was disturbed by the interaction between lithium ions and oxygen atoms. This was because a new bond was formed

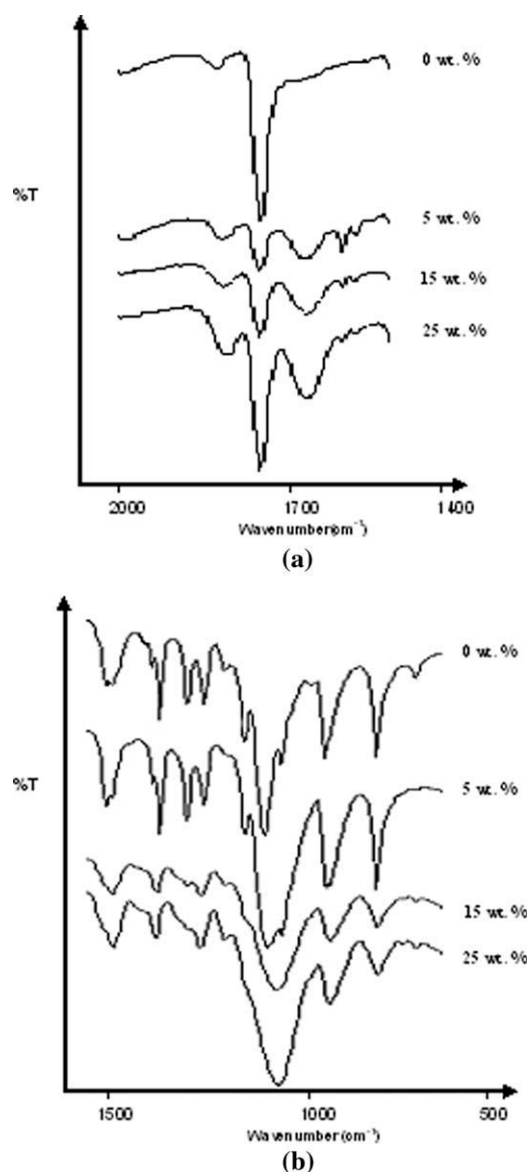


Figure 3 FTIR spectra of PEO-MG49-LiClO₄: (a) carbonyl (C=O) and (b) ether (C—O—C) groups.

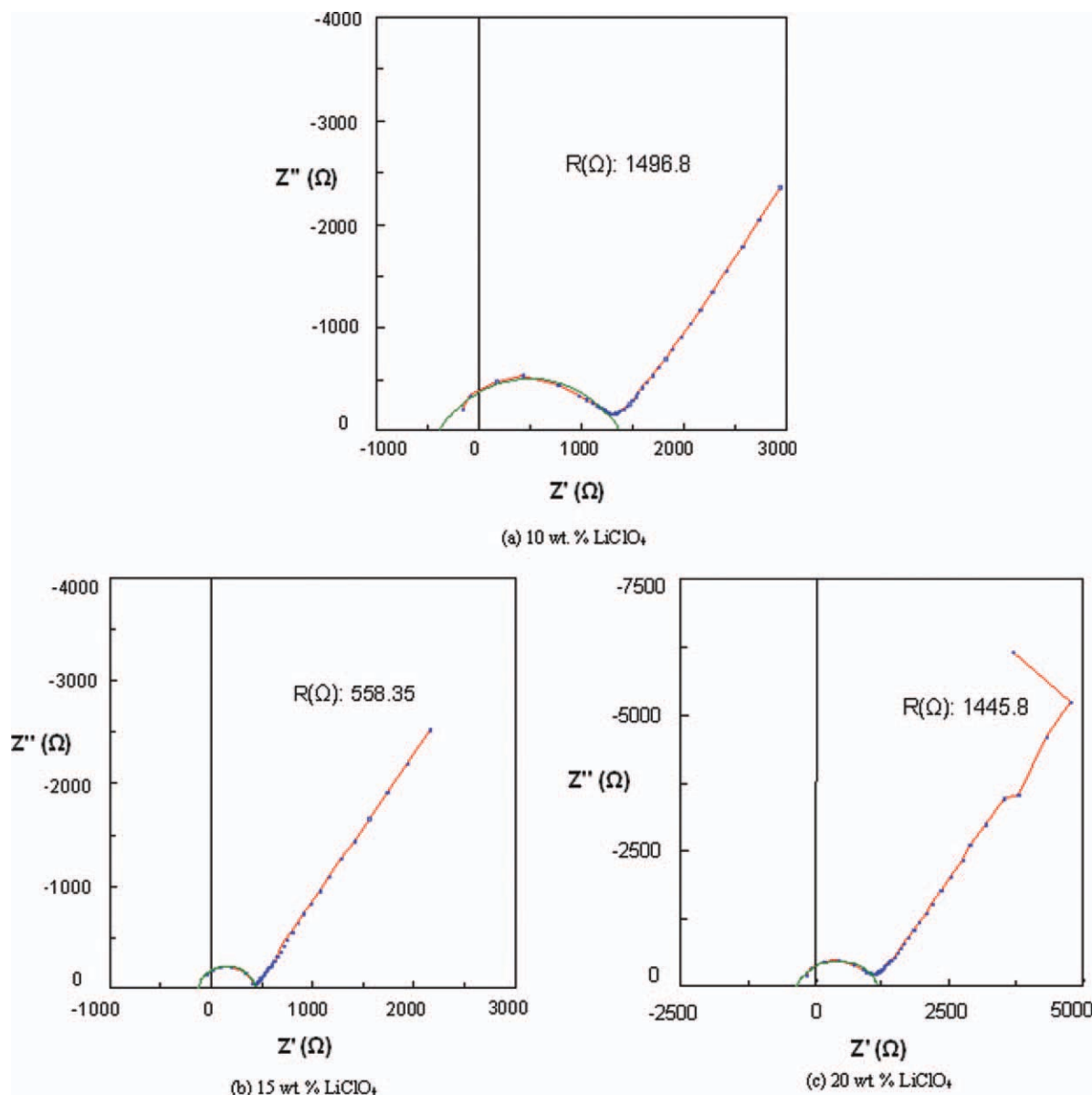


Figure 4 Impedance spectra of PEO–MG49 at (a) 10, (b) 15, and (c) 20 wt % LiClO_4 . Z' is real axis, $Z' (\Omega)$; Z'' is imaginary axis, $Z'' (\Omega)$; $R (\Omega)$ is bulk resistance, $R (\Omega)$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

between lithium ions from the doping salt and oxygen atoms in the structure of the polymer host to form a new bond called a *coordinate/dative bond*; this led to the formation of polymer–salt complexes.²² This interaction affected neighboring bonding in the polymer host to shift from the remaining vibration mode, such as $\nu(\text{CH}_2)$ rocking at 961, 841–949, and 838 cm^{-1} , $\nu(\text{CH}_2)$ twisting at 1278 and 1240–1247 cm^{-1} , and $\nu(\text{CH}_2)$ wagging at 1359 and 1342–1351 cm^{-1} .

Ionic conductivity

The ionic conductivity (σ) was calculated from the bulk resistance (R_b) and was obtained from the intercept on the real impedance axis (Z' axis), the film

thickness (l), and the contact area of the thin film (A), according to the following equation: $\sigma = [l / (AR_b)]$.¹⁶ Figure 4 shows the complex impedance spectrum of PEO–MG49 at 10 wt % LiClO_4 [Fig. 4(a)], 15 wt % LiClO_4 [Fig. 4(b)], and 20 wt % LiClO_4 [Fig. 4(c)]. The complex impedance spectra showed two well-defined regions, a semicircle in the high-frequency range that was related to the conduction process in the bulk of the complex and a linear region in the low-frequency range that was attributed to the bulk effect of blocking electrodes. The curvature was caused by the double layer at the blocking electrodes.^{26,27} The behavior of dielectrics under the application of steady voltage was mainly dependent on the type of contacts between the metal

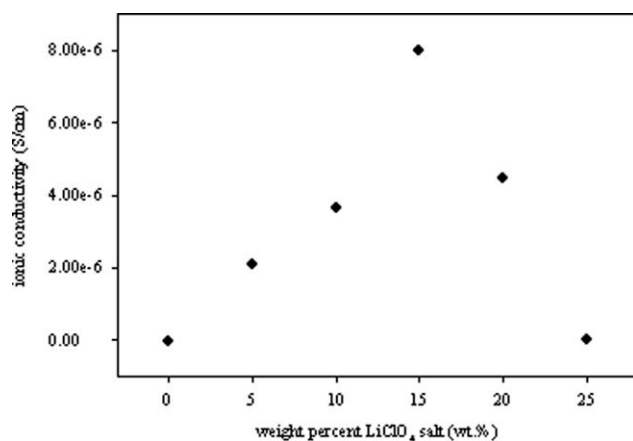


Figure 5 Variation of the ionic conductivity of PEO-MG49 with various weight percentages of LiClO₄.

electrodes and the dielectric material. Therefore, the observed transient current was due to the polarization of the material; this may have been caused by the hopping positive and/or negative charges in the polymer electrolytes system, as reported elsewhere.²⁸

Figure 5 shows the variation of conductivity of PEO-MG49 at various weight percentages of LiClO₄. The ionic conductivity of the PEO-MG49 blend without salt was 4.0×10^{-9} s/cm. The highest ionic conductivity in PEO-MG49-LiClO₄ was 8.0×10^{-6} s/cm at a 15 wt % salt concentration. The presence of 60% PEO increased the conductivity up to two magnitudes in comparison to previous studies on MG49.¹⁶ The ionic conductivity of PEO-MG49-LiClO₄ was still higher compared to that of the PEO-LiClO₄ polymer electrolyte, which was around 10^{-7} to 10^{-8} s/cm, as reported elsewhere,^{2,8,9} and comparable to the result reported by Chu and coworkers.^{6,7}

The ionic conductivity increased as the salt addition increased up to its optimum level in the polymer host. This was attributed to the ion dissociation of LiClO₄ salts into Li⁺ and ClO₄⁻ species. The increase in the number of conducting species in the electrolyte helped to increase the conductivity.^{17,24} This optimum value indicated the maximum and effective interaction between oxygen atoms and Li⁺ ions in the electrolyte. This interaction was explained by FTIR spectroscopy elsewhere.^{13-16,22} It was discovered that a coordinate bond was formed in the complexes between lithium ions and oxygen atoms from the polymer host.

After the optimum conductivity at 15 wt % LiClO₄, we believed that the recrystallization of lithium salt was due to the high salt concentration in the electrolyte system.^{7,19} The high salt concentration gave a high tendency to the ionic species to associate or aggregate with each other.^{21,29,30} This ionic's tendency decreased the number of conducting species

and decreased the ionic mobility. Thus, it congested the ionic migration in the segmental polymer chain. This process disturbed the conducting process in the electrolyte systems and provided low conductivity in the systems.

CONCLUSIONS

A PEO-MG49 SPE with a ratio of 60 : 40 and doped with LiClO₄ was successfully prepared by a solution casting technique. The highest conductivity achieved was 8.0×10^{-6} S/cm at 15 wt % LiClO₄. However, it was still a factor of 100–1000 below that which is necessary for a room-temperature polymer electrolyte. Infrared analysis showed that the interaction between lithium ions from the doping salt and oxygen atoms occurred at the ether group (C–O–C) on the structure of the polymer host. The morphology studies by SEM showed that the surface morphology of the sample changed from rough to smooth with the addition of lithium salts.

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