

Short communication

The role and impact of rubber in poly(methyl methacrylate)/lithium triflate electrolyte

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Abstract

In this research, new thin freestanding films of poly(methyl methacrylate) (PMMA)/50% epoxidised natural rubber (ENR 50) were doped with lithium triflate, LiCF_3SO_3 salt was prepared by a solvent casting method. The incorporation of ENR 50 is found to increase the conductivity of PMMA/ LiCF_3SO_3 by two orders of magnitude at room temperature. The highest conductivity achieved was $5.09 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature when 60% of LiCF_3SO_3 salt was introduced into the PMMA blend containing 10% ENR 50. The formation of excessive hydrogen bonds and interchain crosslinking limit the performance of the blend at higher concentrations of ENR 50. The ionic conduction mechanisms in PMMA/ENR 50/ LiCF_3SO_3 electrolytes obey the Arrhenius rule in which the ion transport in these materials is thermally assisted.

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1. Introduction

PMMA (Fig. 1) is a transparent polymeric material that possesses many desirable properties such as light weight, high light transmittance, chemical resistance, uncoloured, resistance to weathering corrosion and good insulating properties [1]. PMMA has an amorphous morphology and its T_g is 120°C . PMMA has a polar functional group in its polymer chain that exhibits a high affinity for lithium ions and plasticizing organic solvents. Therefore, it displays one of the essential characteristics of a potential polymer electrolyte material. The oxygen atom from its carbonyl group is expected to form a coordinate bond with the lithium ions from the doping salts.

Iijima et al. [2] used PMMA as a polymer host material in the development of a polymer based electrolyte. It was found that, in its gel form, it has given high ionic conductivity at sub-ambient temperature and a good solvent retention ability [3–6].

To date, PMMA-based gel electrolytes have received much attention and have been tested in electrochemical devices [5,6]. These systems have exhibited high ionic conductivity at room temperature and have better interfacial properties towards the lithium electrodes when compared to a PAN based gel [6,7]. Following these studies, several systems based on PMMA has been applied to other applications such as in electrochromic devices [8,9]. Due to its good optical properties, PMMA has become a good candidate for non-linear optical applications in communications technology [10].

The most serious drawback of plasticized gel-based PMMA system is its poor mechanical property [11] and to date this remains unsolved. Mechanical properties can only be improved by modifying the polymer–solvent ratio. However, these will adversely affect the conductivity of the material. Another serious problem is facing PMMA/PC systems in which, the presence of PC can easily corrode the lithium metal anode in an electrochemical cell [6]. High ionic conductivity of $10^{-4} \text{ S cm}^{-1}$ can only be reached at about 100°C [12].

Blending the polymer with another polymer can circumvent problems associated with poor mechanical properties. Furthermore, the blending approach can form a freestanding PMMA-

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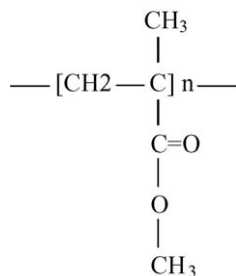


Fig. 1. Structure of PMMA.

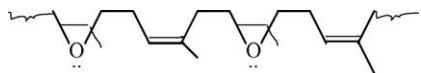


Fig. 2. Structure of ENR 50.

based electrolyte film and therefore provide good mechanical properties. Rhoo et al. [11] verified the blend concept in PVC/PMMA electrolyte systems. Also, Kim and Oh [13] demonstrated the use of a PVC/PMMA blend in lithium ion polymer battery. The mechanical strength of PMMA is increased as the content of PVC is increased. However, the conductivity of the system is decreased due to poor adhesion that leads to increase of interfacial resistance.

In this work the main polymer host, poly(methyl methacrylate) (PMMA) is blended with 50% epoxidised natural rubber (ENR 50) (Fig. 2). This modification should lower the glass transition temperature, T_g of PMMA and also give a rubber-like characteristic to the new material, good elasticity and adhesion, which therefore could provide excellent contact between the electrode and the electrolyte in batteries.

In this work solid PMMA-based electrolytes in a form of thin free standing films are fabricated. Since PMMA alone forms a brittle film, 50% epoxidised natural rubber (ENR 50) was added to reprove the brittle properties of PMMA films and hence produce the soft elastomeric, good elasticity and adhesion properties of a freestanding PMMA film. With these characteristics, it is predicted to give excellent contact between an electrolytic layer and an electrode in batteries.

2. Experimental

2.1. Materials

PMMA (ALDRICH, $M_w = 120,000$), tetrahydrofuran, THF (MERCK), and LiCF_3SO_3 (ALDRICH) were used without further purification. ENR 50 was obtained from Guthrie Polymer Sdn. Bhd. Siliau, Negeri Sembilan, Malaysia.

2.2. Preparation of blends

PMMA and ENR 50 stock solutions were prepared separately by dissolving the polymers in THF by continuous stirring with a magnetic stirrer. The two polymer solutions were then mixed in a beaker together with the LiCF_3SO_3 salt. The concentration of PMMA was fixed in all sample preparations. The concentration

of ENR 50 added was 10% and 20% of PMMA by weight. The amount of LiCF_3SO_3 salt added to each PMMA solution containing 10% and 20% ENR 50 was 20%, 40% and 60% of the weight of PMMA. Solutions were stirred for about 24 h. All the preparation steps were done in a glove box. The electrolyte solutions were then cast onto glass Petri dishes and left to dry by solvent evaporation at room temperature. The films obtained were further dried in an oven at 50°C for another 48 h. The solvent free films were then kept in a desiccator until further use.

2.3. Measurements

2.3.1. FT-IR analysis

The FT-IR analysis was carried out using a SHIMADZU FT-IR 8300 Fourier transform infra red spectrophotometer which was used to perform IR analysis on PMMA/ENR 50 blends and their complexes in the frequency range of $4000\text{--}400\text{ cm}^{-1}$.

2.3.2. Impedance spectroscopy

To measure the impedance of the films, the samples were cut into a round shape that fit the size of the electrodes. The samples were then sandwiched between the two stainless steel blocking electrodes with a diameter of 2 cm. A Hioki 3532-50 LCR HiTester was used to perform the impedance (Z) measurement for each electrolyte films over the frequency range of $100\text{ Hz--}1\text{ MHz}$. From the Cole–Cole plots obtained, the bulk resistance, R_b of each sample was determined and hence the conductivity (σ) of the samples were then calculated using $\sigma = l/R_b A$; where l is the sample thickness (cm), A the effective contact area of the electrode and the electrolyte (cm^2), and R_b is the bulk resistance (Ω).

3. Results and discussion

The PMMA/ENR 50 blend produced thin, transparent and flexible freestanding films when doped with LiCF_3SO_3 salt. However, phase separation was observed on the surface of the films, which showed that the blending is not homogeneous.

3.1. FT-IR study

Fig. 3 shows the FT-IR spectrums for pure PMMA, ENR 50, the blend and doped PMMA/ENR 50 films. We will concentrate most on the C=O , O--CH_3 , C--O and --CH_3 bands of PMMA and the epoxide group (--C--O--C--) of ENR 50 in the FT-IR spectrums of the blend films. These groups were expected to be the coordinating sites for the lithium ion.

The C=O band at 1710.7 cm^{-1} of PMMA was not affected by the presence of ENR 50 in 10% ENR 50 blend. However, in 20% ENR 50, the band shifted to lower frequency, i.e. 1706.9 cm^{-1} . However, the O--CH_3 , C--O , and --CH_3 bands of PMMA at 1388.7 , 2950.9 and 1438.8 cm^{-1} respectively were found shifted in both blend.

On the other hand, the C--O--C-- and C=C band of ENR 50 at 1250.8 and 1660 cm^{-1} respectively were found to be absent in both blends. Therefore, it can be assumed that the opening

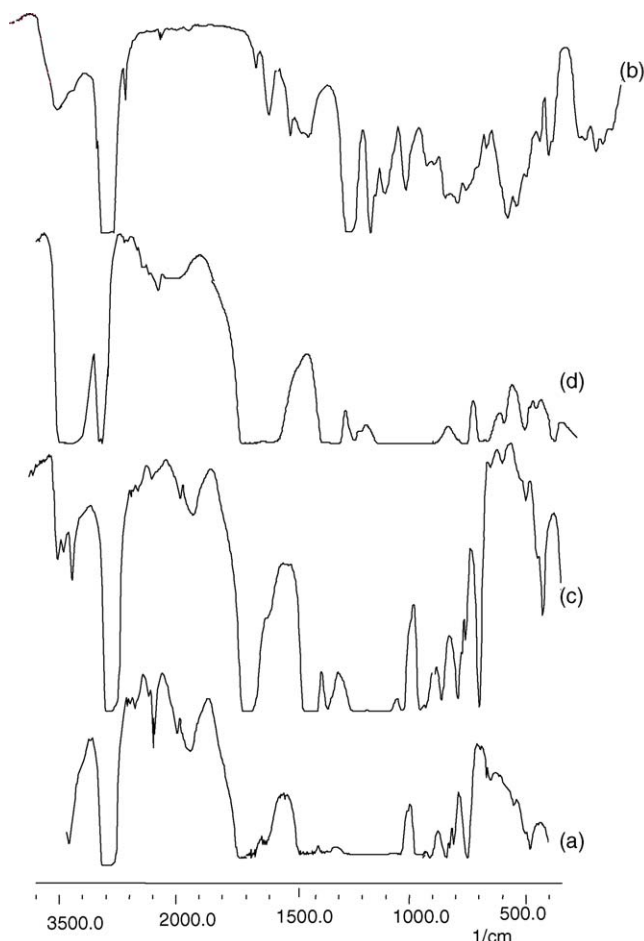


Fig. 3. FT-IR spectrums for (a) pure PMMA, (b) pure ENR 50, (c) 10% ENR 50 blend, and (d) 10% ENR 50 blend doped with 20% LiCF_3SO_3 salt.

of the double bond in ENR 50 may be due to the formation of interchain cross linking in the system.

The broad band observed at $4000\text{--}3500\text{ cm}^{-1}$ in the FT-IR spectrum of PMMA/ENR 50, supports the presence of hydrogen bonds between and within polymer chains. Therefore, it can also be concluded that the PMMA/ENR 50 blend is partially compatible via hydrogen bonds. The above analysis confirmed that interactions occurred between PMMA and ENR 50 in the blend. The interaction can occur via hydrogen bonding between PMMA and ENR 50 chain as explained above.

It is observed that a small shoulder at ~ 1360 and $\sim 1033\text{ cm}^{-1}$ are observed in the FT-IR spectra of the PMMA/ENR 50 blend when LiCF_3SO_3 salt is added into the system. These vibrational bands can be assigned to CF_3 and a non-degenerate vibrational mode of $\nu(\text{SO}_3)$ from free triflate anions, respectively. It is observed that the shoulder of CF_3 became weak and the $\nu(\text{SO}_3)$ slightly broadened and shifted as the amount of salt is increased. This indicates the formation of ion pairs or ion aggregates as the number of ions is increased. Furthermore the carbonyl bands at $\sim 1700\text{ cm}^{-1}$ in both blends are observed to broaden due to the interaction that occurs between the carbonyl groups. The $-\text{O}-\text{CH}_3$ and $-\text{CH}_3$ bands are also shifted in both blends. From these observations, it is confirmed the formation of polymer–salt complexes in the electrolyte films occur via coordinate bonds.

3.2. Ionic conductivity

Overall, the conductivity of the PMMA/ENR 50 blends are higher than in their individual pure form when doped with the same amount of LiCF_3SO_3 salt (40%). The ENR 50 may have played the role of a “plasticizer” to reduce the viscosity of the PMMA chains hence increasing the chain mobility. On the other hand PMMA may act as a “mechanical stiffener” for ENR 50. ENR 50 has previously acted as a plasticizer in the ENR 50/PVC blend [14], which is found to reduce the stiffness of PVC.

It is noted that the 10% ENR 50 blend presented higher conductivity values compared to the 20% ENR 50 blend at all compositions. Increasing the amount of ENR 50 in the blend will increase the number of reactive epoxide groups that have a potential to form hydrogen bonds. The formation of excessive numbers of hydrogen bonds may also reduce the segmental motion of the polymers that are responsible for the transport of lithium ions. Furthermore, increasing the number of ENR 50 molecules may induce interchain crosslinking and hence develop a more highly viscous phase in the blend matrix. Besides reducing chain segment mobility, the occurrence of this highly viscous phase may retard the migration of lithium ions in the blend matrix. Increasing the concentration of ENR 50 in the blend may also increase the number of oxygen atoms contributed from the epoxide groups. According to Glasse et al. [15], they may also cause excessive coordination sites for the lithium ion that hinder the migration of the ions along the polymer chain.

The highest conductivity achieved is $5.09 \times 10^{-5}\text{ S cm}^{-1}$ at room temperature when 60% of LiCF_3SO_3 salt is introduced in the PMMA blend containing 10% ENR 50 (Fig. 4). It is observed that the highest conducting sample at room temperature for PMMA/ENR 50/ LiCF_3SO_3 , PE1T3 also exhibited the highest electrical conductivity at all temperatures. The highest conductivity of 10^{-4} S cm^{-1} can also be achieved at 359 K from this sample.

The plot of $\ln(\sigma T)$ versus $1000/T^{-1}$ (Fig. 5) for the PMMA/ENR 50 blend with various amounts of LiCF_3SO_3 salt exhibits a straight line. This indicates that the plot of $\ln(\sigma T)$ versus $1000/T^{-1}$ for PMMA/ENR 50/ LiCF_3SO_3 electrolytes obey the Arrhenius rule in which the ionic conduction in these materials is thermally assisted.

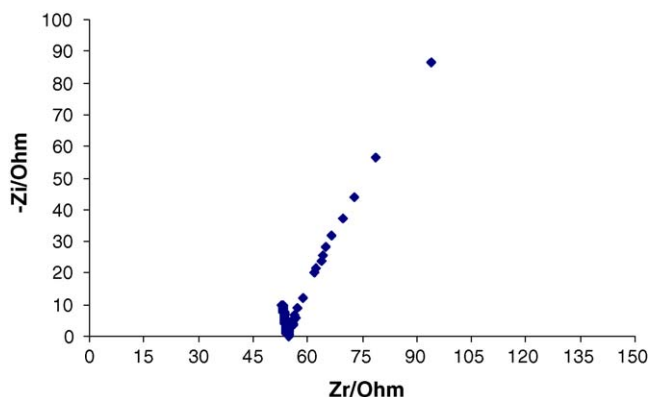


Fig. 4. The Cole–Cole plots for the highest conducting sample: PE1T3.

Table 1
The average conductivity of PMMA/ENR 50/LiCF₃SO₃ at various composition and temperatures

ENR 50 (%)	LiCF ₃ SO ₃ (%)	Sample	Conductivity, σ ($\times 10^{-7}$ S cm ⁻¹)						E_a ($\times 10^{-1}$ eV)
			T (± 2 K)						
			299	309	319	329	339	349	
0	40	–	0.488	1.77	2.25	4.72	8.35	13.3	–
10	20	PE1T1	0.0059	0.0064	0.0067	0.0071	0.0072	0.0083	0.942
	40	PE1T2	20.7	41.6	60.1	107	154	248	4.53
	60	PE1T3	509	807	1010	1330	1680	2220	2.85
20	20	PE2T1	0.56	0.64	0.71	0.74	0.87	1.01	1.308
	40	PE2T2	6.27	11.4	18.2	31.6	50.1	78.8	4.771
	60	PE2T3	119	218	300	342	408	865	3.37
100	40	–	0.058	0.085	0.10	0.13	0.18	0.22	–

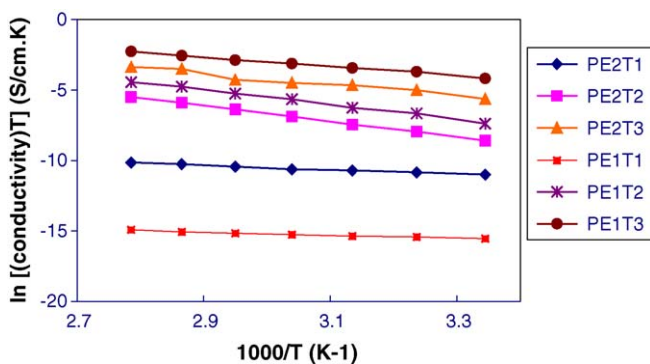


Fig. 5. Arrhenius plot for different amount of LiCF₃SO₃ in PMMA/ENR 50/LiCF₃SO₃ electrolyte.

From Fig. 5, the activation energy, E_a , for the salted PMMA/ENR 50 blend is calculated from the gradient of the Arrhenius plots. It is observed that both 10% and 20% ENR 50 exhibit the same E_a trend in which the E_a increased as the amount of salt was increased up to 40% after which the E_a decreased. Note that the activation energy is the combination of the energy of defect formation and the energy of defect migration. Therefore it can be suggested that the rise in the E_a is due to the energy that is required to provide a conductive condition for the migration of ions. However, PE1T3 and PE2T3 offer a better environment hence require less energy for the ion transport. It is found that the 20% ENR 50 blend exhibits the highest E_a at all compositions. This may be due to the presence of a highly crosslinked viscous phase in 20% ENR 50, that hampers the ionic motion from one site to another. Table 1 summarizes the average conductivity and the respective E_a values of PMMA/ENR 50/LiCF₃SO₃ at various compositions.

4. Conclusions

PMMA/ENR 50 blend films exhibited a conductivity two to three orders of magnitude higher than in their individual

forms when doped with LiCF₃SO₃ salt. The highest conductivity achieved was 5.09×10^{-5} S cm⁻¹ at room temperature when 60% of LiCF₃SO₃ salt is added to the PMMA film containing 10% ENR 50. The formation of excessive hydrogen bonds and interchain crosslinking, limit the performance of the blend at higher concentrations of ENR 50.

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