

# The Effect of 1-Ethyl-3-Methylimidazolium Acetate on the Structural, Morphological and Electrical Properties of Poly (methyl methacrylate) (PMMA)-based Electrolyte Films

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## ABSTRACT

*In this study, the ionic liquid (IL) of 1-ethyl-3-methylimidazolium acetate, [EMIM][Ac] was incorporated into the PMMA-based electrolyte via solution casting technique. Lithium triflate (LiTf) was also doped into the system to provide additional charge carrier. The effect of various amount [EMIM][Ac] towards the structural, morphological, and electrical properties of PMMA-based PE films were determined using Fourier transform infrared spectroscopy (FTIR), optical microscope (OM) and electrochemical impedance spectroscopy (EIS) respectively. Solid, flexible, and free-standing films of PMMA-based electrolyte were successfully obtained after the addition of IL. As confirmed from FTIR analyses, there occurs interaction between the oxygen atoms of PMMA with the imidazolium cation of the IL. With the addition of IL, the ionic conductivity was also observed to increase which can be related to the large structure of IL that occupy the space between PMMA chain hence reduced the formation of hydrogen*



*bonding. This has been further confirmed by the OM analyses which showed the increase in grain size for the modified PMMA system after the doping of IL. The highest conductivity of  $9.86 \times 10^{-7} \text{ S cm}^{-1}$  was obtained when 42 wt.% IL (PMMAIL5) was incorporated into the PMMA-based electrolyte system. This is due to the increase in the amorphosity of the sample which improved the ion diffusion within the polymer complex. The increase in the amorphosity of the sample is confirmed by the reduced in the number of grains as observed in the optical micrograph of PMMAIL5.*

*Keywords: PMMA; Ionic Liquid; Polymer Electrolytes; Thin Film; Flexible Film*

## INTRODUCTION

Polymers are used in wide range of industries, including automotive, agricultural, aerospace, electronics, and medical devices [1]. The use of polymer as an electrolyte in electrochemical devices is the focus of this research. This type of polymer is called as polymer electrolyte (PE). PE is a membrane made up of salts dissolved in a high-molecular-weight polymer matrix [2]. PEs have many advantageous characteristics such as great mechanical strength, light in weight, excellent ionic conductivity, wide electrochemical stability, and high energy density [3].

Polymer host is required in the preparation of polymer electrolytes as it serves as a base matrix prior to the incorporation of any other components. Polymer hosts that have been extensively researched are poly(ethylene oxide) (PEO) [4], poly(vinyl alcohol) (PVA) [5] and poly(methyl methacrylate) (PMMA) [6]. Among them, PMMA has the highest electrolyte-electrode interface stability [6]. Therefore, in this study, PMMA has been used as a polymer host. The stability towards the lithium electrode can be obtained only when PMMA is fabricated in the form of thin film [7]. However, PMMA-based electrolytes films are brittle, resulting in poor adhesion to the electrode and increased ionic conduction resistance. The brittleness [7] of PMMA-based electrolyte film can be attributed to its polarity, which causes interchain crosslinking via hydrogen bonding and limits the polymer chain flexibility. Several techniques, such as polymer blending, addition of plasticizers and organic fillers have been used to enhance the

brittleness of PMMA-based electrolyte film. However, these techniques were ineffective due to low mechanical properties caused by higher amount of plasticizer, agglomeration caused by filler, and film immiscibility during the polymer blending procedure [7]. Recently, it has been reported that the incorporation of IL such as 1-methyl-3-pentamethyldisiloxymethylimidazolium bis(trifluoromethylsulfonyl)imide ( $[(\text{SiOSi})\text{C}_1\text{C}_1\text{im}][\text{NTf}_2]$ ) has improved the brittleness of PMMA-based electrolyte films [7]. This was due to the bulky structure of IL which occupied the space between PMMA chains hence inhibited the formation of hydrogen bonding. The highest ionic conductivity obtained for this system was  $2.65 \times 10^{-4} \text{ Scm}^{-1}$  which is higher if compared to conductivity of pure PMMA films. However, the ionic conductivity obtained is still low if compared to liquid electrolytes. The low ionic conductivity might be due to restriction in the movement of ions due to the bulky structure of  $[(\text{SiOSi})\text{C}_1\text{C}_1\text{im}][\text{NTf}_2]$  (Mw: 523.62 g/mol) [8]. This agrees with the study done by Syairah et al. [9] which reported that the ionic conductivity of PE was also influenced by the structure of IL.

Therefore, the IL with less bulky structure and lower molecular weight namely 1-ethyl-3-methylimidazolium acetate  $[\text{EMIM}][\text{Ac}]$  (Mw: 170.21 g/mol) [10] was used in this study.  $[\text{EMIM}][\text{Ac}]$  was added into the PMMA electrolytes to produce PMMA-based electrolyte films which are flexible, free-standing, and highly conducting. The lithium triflate (LiTf) was also doped into the PMMA system to provide additional conducting ions. To further understand the properties of the prepared PMMA-based electrolyte, the structural, morphological, and electrical properties of the system were further investigated.

## METHODOLOGY

### Preparation of Films

To prepare the PE films, solution casting technique was adapted from the study done by Zailani et al. [7]. 0.5 g PMMA and 0.2 g LiTf were dissolved in 50 mL of THF for 24 h using magnetic stirrer. The mixture was casted onto the Petri dish and left at room temperature for 24 h or until the formation of film. Next, 0.5 g of PMMA, 0.2 g of LiTf and 13 wt.% of IL were dissolved in 50 mL of THF using magnetic stirrer. The mixture was

casted onto the petri dish and left at room temperature for 24 h or until the formation of film. The same steps were repeated by incorporating different wt.% of IL (i.e.: 23, 31, 37 & 42 wt.%) (Table 1) into the electrolyte system. All the dried films were peeled off and stored in the oven for a few h at 40 °C. Lastly, before further characterizations, the films were stored in desiccators.

**Table 1: The composition of PMMA-based PE system**

Weight of PMMA (g)	Weight of LiTf (g)	Amount of IL (wt. %)	Weight of IL (g)	Symbol
0.5	0	0	0	PMMA
	0.2			PMMAIL0
		13	0.1027	PMMAIL1
		23	0.2054	PMMAIL2
		31	0.3081	PMMAIL3
		37	0.4108	PMMAIL4
		42	0.5135	PMMAIL5

### Fourier transform infrared spectroscopy (FTIR)

FTIR (Thermo Fisher Scientific Nicolet iS 10) with Attenuated Total Reflectance (ATR) was used to determine the interactions between PMMA, LiTf and IL. The PMMA-based electrolyte film was placed onto the crystal. Then, the measurement was taken in the frequency range of 4000-600  $\text{cm}^{-1}$  with 2  $\text{cm}^{-1}$  resolutions and 16 scans.

### Optical microscopy (OM)

Optical microscope (Nikon ECLIPSE ME 600) was used to observe the morphology of the PMMA-based electrolyte films. The sample was placed on a microscope slide and the image was captured at 10x magnification.

### Electrochemical impedance spectroscopy (EIS)

Using EIS (HIOKI 35232-01 LCR), the impedance of the PMMA-based electrolyte films was measured at a frequency range of 100 Hz – 1 MHz at room temperature. Firstly, the thickness of the film was measured using micrometre screw gauge. Then, the polymer electrolyte film was sandwiched between the two stainless steel blocking electrodes before

the impedance measurement was taken. The bulk resistance ( $R_b$ ) value for each sample was obtained from the Cole-cole plot generated after the measurement. The ionic conductivity was calculated using Eq. (1).

$$\sigma = \frac{l}{R_b \cdot A} \quad (1)$$

Where  $l$  is the electrolyte sample thickness (cm) and  $A$  is the electrode-electrolyte contact area (cm<sup>2</sup>).

## RESULTS AND DISCUSSION

The preparation of the PMMA-based electrolyte films with addition of lithium salt, LiTf and IL, [EMIM][Ac] was successfully done. The films obtained for pure PMMA and PMMA/LiTf (PMMAIL0) were brittle. This might be due to the interchain crosslinking via hydrogen bonding that occurred between polar PMMA chains. This has been also observed in the study by Zailani et al. [7]. Solid, flexible, and free-standing films were successfully obtained after 13 – 42 wt.% of IL (PMMAIL1 – PMMAIL5) were added into the PMMA/LiTf film. This indicates that the bulky structure of IL had reduced the interchain crosslinking by occupying the space between the polymer chains. The same observation was also reported by the study on PMMA/[(SiOSi)C<sub>1</sub>C<sub>1</sub>im][NTf<sub>2</sub>] done by Zailani et al. [7].

### FTIR studies

Figure 1 shows the FTIR spectra for IL, pure PMMA and PMMAIL0-PMMAIL5. After the addition of LiTf into the PMMA, the new peak representing LiTf appeared at 1033 cm<sup>-1</sup> (SO<sub>3</sub> stretching) for PMMAIL0. The appearance of this peak shows that LiTf was successfully incorporated into the PMMA matrix. The effect of the addition of LiTf was observed by the shifting of C=O stretching and O-CH<sub>3</sub> bend peaks of PMMA from 1724 cm<sup>-1</sup> to 1714 cm<sup>-1</sup> and from 1447 cm<sup>-1</sup> to 1450 cm<sup>-1</sup> respectively. This confirmed that interaction has occurred between the oxygen atoms of PMMA with the Li<sup>+</sup> of the salt. The same observation was also reported for the study on PMMA/Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>/EC electrolyte done by Ramesh et al. [5].

Upon addition of IL into the PMMA/LiTf, the new peaks representing IL appeared at  $\sim 1150\text{ cm}^{-1}$  (C-O stretching) and  $\sim 1566\text{ cm}^{-1}$  (C-N stretching). Similar observation was reported by Dhupal et al. [11]. This indicates that IL was successfully incorporated into the PMMA/LiTf matrix. The effect of the incorporation of IL into PMMA matrix was observed by the shifting of the C=O stretching peaks from  $1714$  to  $1724\text{ cm}^{-1}$  with reduced in their intensities. Meanwhile, there was no change in the wavenumber for OCH<sub>3</sub> bend ( $\sim 1442\text{ cm}^{-1}$ ), but the reduced in their peak intensities were observed. These changes indicate that the interaction between the two potential coordinating sites of PMMA and the imidazolium cation of the IL has occurred. The same observation was also reported for the study on PMMA/LiTFSI/IL electrolyte done by Li et al. [12]. The possible interactions between PMMA, LiTf and IL was illustrated as in Figure 2.

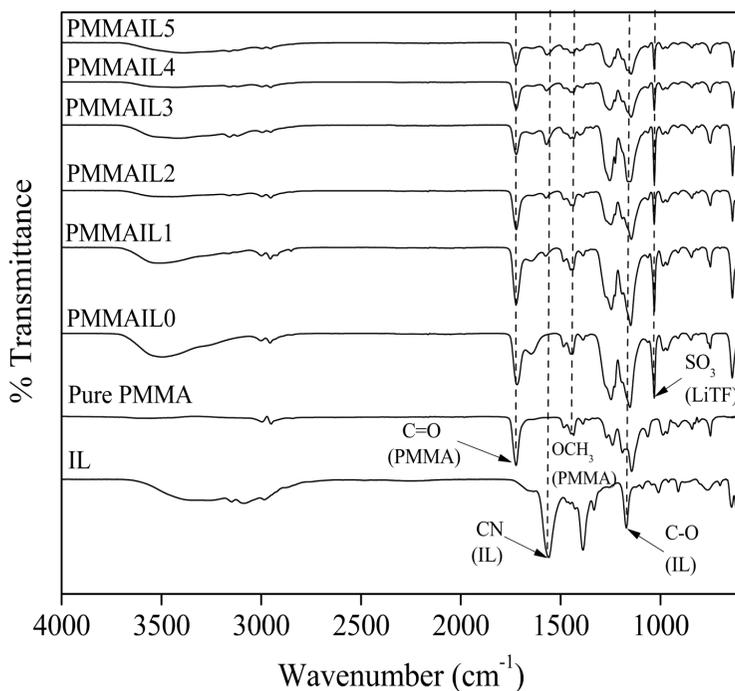


Figure 1: FTIR spectra for IL, pure PMMA and PMMAIL1-PMMAIL5

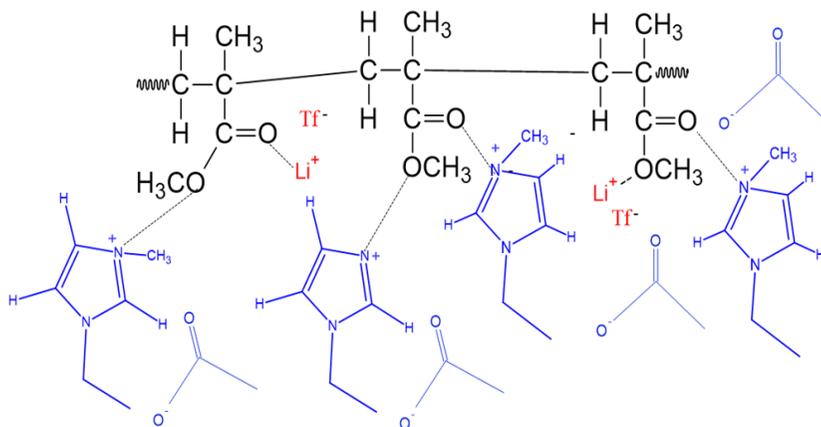


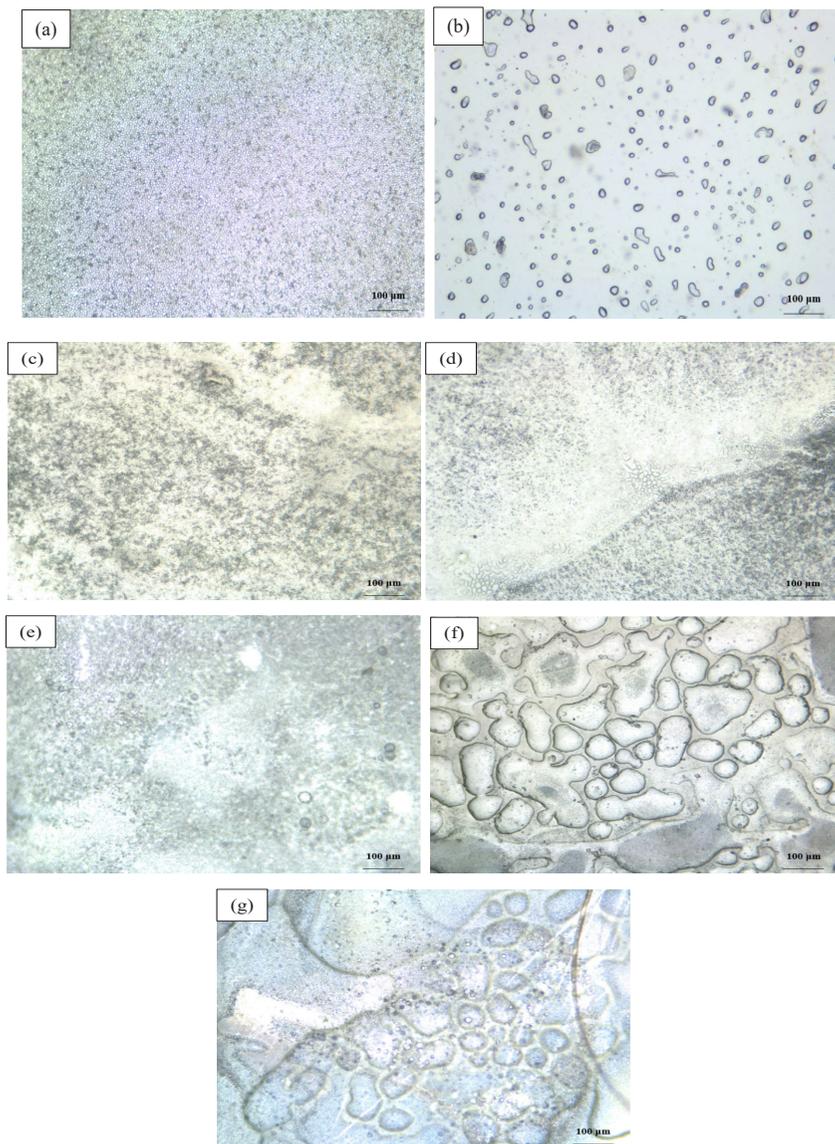
Figure 2: Possible interactions between PMMA, LiTf and IL

## Morphological studies

The surface morphologies of the PMMA/LiTf/IL films were observed using the optical microscope (OM) at 10x magnification. Figure 3(a) shows the morphology for pure PMMA film that shows granule-like structure with random orientation. It was observed that there were more grains available in PMMA film if compared to other samples, hence explaining its brittle structure. After the addition of lithium salt into the PMMA matrix, the morphology of PMMAIL0 (Figure 3(b)) shows reduction in the number of the grains. This is because the interaction has occurred between the oxygen atoms of PMMA with the  $\text{Li}^+$  of the salt as confirmed by FTIR analysis.

After the addition of IL, the increase in grain size was observed to occur for selected grains in PMMAIL1-3 (Figure 3(c)–(e)) and it was occurring to most of the grains in PMMAIL4-5 (Figure 3 (f)–(g)). The increase in grains' sizes can be related to the successful encapsulation of IL hence reducing the interchain crosslinking between PMMA chains. This observation was also reported in the study of PMMA/ $[(\text{SiOSi})\text{C}_1\text{C}_1\text{im}][\text{NTf}_2]$  done by Zailani et al. [7]. On the other hand, the morphology of PMMAIL3 somehow shows a few clumps which might be due to excess salt or IL. Apart from that, the number of grains available in the PMMAIL4-5 system was observed to greatly reduce due to the merging between the neighbouring grains. The

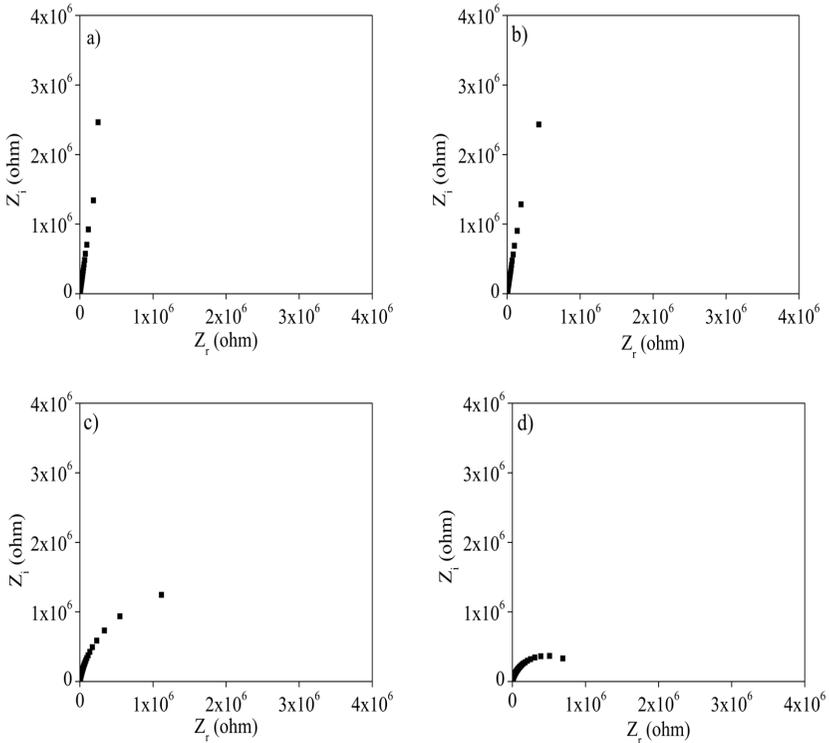
reduce number of grains contributes to the increase in the amorphousity of the samples hence explained the higher flexibility of the film.

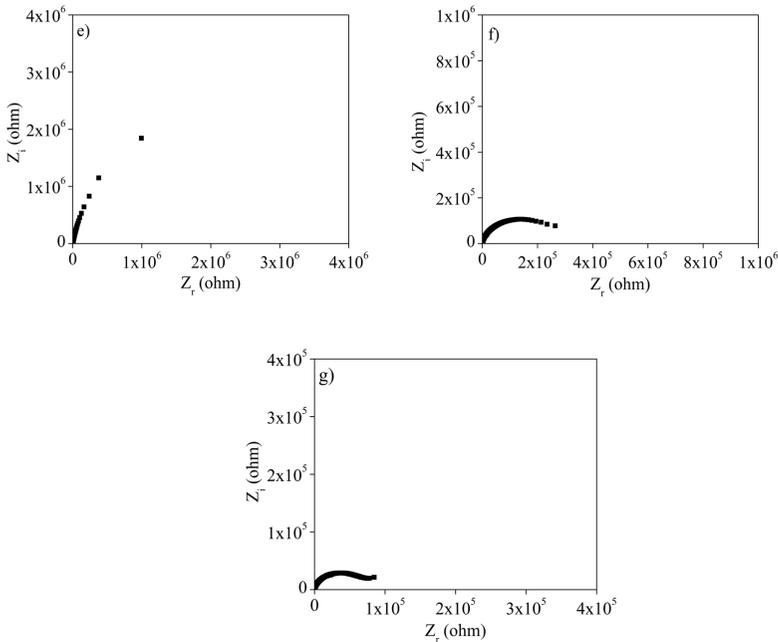


**Figure 3: Optical micrographs for (a) PMMA, (b) PMMAIL0, (c) PMMAIL1, (d) PMMAIL2, (e) PMMAIL3, (f) PMMAIL4 and (g) PMMAIL5**

## Conductivity studies

Figure 4 shows Cole-cole plot obtained for each sample after EIS measurement. For pure PMMA and PMMAIL0-3, the plots exhibited half semicircles (Figure 4(a)-(e)) while the plots for PMMAIL4-5 exhibited depressed semicircles (Figure 4(f)-(g)) at high frequencies region. The appearance of semicircles indicates that ion migration has occurred in the bulk system [13] hence confirming that all the PMMA/LiTf/IL films are ionic conductors. Furthermore, the appearance of a spike in the lower-frequency range for the Cole-cole plots of PMMAIL2 and PMMAIL 4-5 indicates the ion diffusion in the samples [14]. The appearance of spike with the highest slope in PMMAIL5 implies the faster ion diffusion if compared to other samples. This is due to its amorphous nature, as shown in its optical micrograph (Figure 3 (g)).



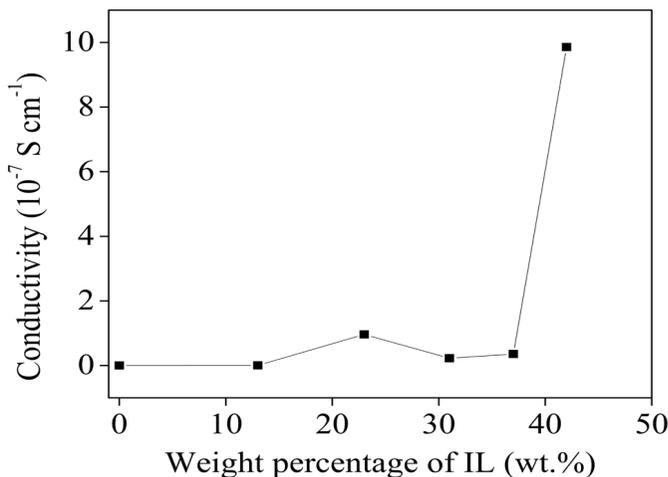


**Figure 4: Cole-cole plots for (a) PMMA, (b) PMMAIL0, (c) PMMAIL1, (d) PMMAIL2, (e) PMMAIL3, (f) PMMAIL4 and (g) PMMAIL5**

The  $R_b$  was determined from the intercept of the spike with the extrapolation of the semicircular region on  $Z_r$  axis. Then, the ionic conductivity was calculated using Eq. (1). Table 2 lists the ionic conductivity values for PMMA/LiTf/IL systems while Figure 5 shows the plot of ionic conductivity versus weight percentage of IL.

**Table 2: Ionic conductivity for PMMA/LiTf/IL system.**

PMMA/LiTf/IL System	Ionic Conductivity (S cm <sup>-1</sup> )
PMMA	1.48 x 10 <sup>-9</sup>
PMMAIL0	2.23 x 10 <sup>-9</sup>
PMMAIL1	6.95 x 10 <sup>-9</sup>
PMMAIL2	9.63 x 10 <sup>-8</sup>
PMMAIL3	2.27 x 10 <sup>-8</sup>
PMMAIL4	3.56 x 10 <sup>-8</sup>
PMMAIL5	9.86 x 10 <sup>-7</sup>



**Figure 5: Plot of ionic conductivity versus weight percentage of IL (wt.%)**

It was observed that the ionic conductivity increased with the addition of 13 – 23 wt.% of IL (PMMAIL1-2). This can be related to the bulky structure of IL, which reduced the formation of hydrogen bonding by occupying the space between PMMA chains, as confirmed from OM analyses. When 31 wt.% of IL (PMMAIL3) was added, the ionic conductivity decreased. The decrease in ionic conductivity could be attributed to the formation of ion multiples or ion aggregates, which decreases the quantity of mobile ions and limits their mobility in polymer complexes. This observation has been further supported by the observed clumps in its optical micrograph (Figure 3(e)). The ionic conductivity then increased again for addition of 37 and 42 wt.% of IL (PMMAIL4-5). This is due to the increase in the amorphousity of the samples attributed by the reduced in the number of grains as confirmed by OM analyses.

The highest ionic conductivity obtained was  $9.85 \times 10^{-7} \text{ Scm}^{-1}$  for PMMAIL5 system. This is due to the increase in the amorphousity of the sample which then improved the ion diffusion within the polymer complex. This has been further confirmed by the appearance of spike with the highest slope for Cole-cole plot of PMMAIL5 (Figure 4(g)). The highest ionic conductivity obtained for this system was comparable to several other

PMMA-based polymer electrolyte system as shown in Table 3. However, the ionic conductivity is lower if compared to the PMMA/[(SiOSi)<sub>2</sub>C<sub>1</sub>C<sub>1</sub>im]<sub>2</sub>]/LiTf system (i.e.:  $2.65 \times 10^{-4} \text{ Scm}^{-1}$ ) which used bulkier IL with higher molecular weight. This is probably due to the inability of the less bulky structure of [EMIM][Ac] to disrupt the hydrogen bonding between PMMA chains.

**Table 3: The Ionic Conductivities for Other PMMA-based Electrolyte Systems**

Polymer electrolyte system	Conductivity ( $\text{Scm}^{-1}$ )	References
PMMA/[(SiOSi) <sub>2</sub> C <sub>1</sub> C <sub>1</sub> im] <sub>2</sub> ]/LiTf	$2.65 \times 10^{-4}$	[7]
PMMA /ENR50 /LiBF <sub>4</sub> /SiO <sub>2</sub>	$5.26 \times 10^{-7}$	[15]
PEO/PMMA/LiTFSI/Al <sub>2</sub> O <sub>3</sub>	$9.39 \times 10^{-7}$	[16]

## CONCLUSION

In this study, solid, flexible, and free-standing films of PMMA-based polymer electrolytes were successfully obtained by the doping of 13 – 42 wt.% IL, [EMIM][Ac] into the PMMA matrix. The interaction between PMMA and IL was discovered to take place between the oxygen atoms of PMMA with the imidazolium cation of the IL as proven from FTIR analysis. With the addition of IL, the ionic conductivity was also observed to increase if compared to the non-modified PMMA/LiTf system. This can be attributed to the bulky structure of IL, which occupies the space between PMMA chains, reducing the formation of hydrogen bonding. The highest conductivity of  $9.86 \times 10^{-7} \text{ Scm}^{-1}$  was obtained for PMMAIL5, and this is due to the increase in the amorphosity of the sample, which then improved the ion diffusion within the polymer complex. The increase in the amorphosity of the sample can be confirmed by the reduced in the number of grains as observed in the optical micrograph of PMMAIL5. For further studies, the effect of other different molecular weight ionic liquids on the properties of PMMA-based PE can be carried out.

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