# CHARACTERISTICS OF PMMA–GRAFTED NATURAL RUBBER POLYMER ELECTROLYTES

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DEPARTMENT OF PHYSICS
FACULTY OF SCIENCE
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KUALA LUMPUR
2012

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THESIS SUBMITTED FOR FULFILLMENT OF THE
REQUIREMENT FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS
FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR
2012

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# ACKNOWLEDGEMENT

First and foremost, I wish to express my great appreciation to Professor Dr. Abdul Kariem Bin Mohd Arof, my supervisor for his invaluable guidance, support and encouragement throughout this research work. This work would not have been a reality without his sparking ideas and worthy words. I am humbly thankful to him for his remarkable supervision and attention.

I also would like to thank my co-supervisor, Dr. Siti Rohana binti Majid for her help, guidance and advices throughout this work. Thanks for being understanding and supportive.

I would like to wish my deepest thank you to all at the Centre for Ionics University of Malaya. My appreciation to Dr. S. Ramesh, Dr. K. Ramesh, Dr. Zul Hazrin and Dr. Abubaker for their neverending help and guidance in my experimental work. To my friends: Aida, Aini, Din, Fitriah, Hamdi, Mior, Leeana, Leena, Shujahadeen, Sim, Teo, Thompson, Jimmy, Jun, Kak Mazni, Nabila, Wani, and Zila. I most appreciate your cooperation, team work, and most importantly, friendship.

To Encik Ismail Che Lah (assistant science officer of our centre), Shahril (SEM), Pakcik Mat (XRD), Endang (FTIR) and others in the Department of Physics, thank you for your kindness and cooperation for helping me towards completing my experiments.

Last but not least, my gratitude and appreciation to my family especially to my father (Yap Shio Chuan), mother (See Fong Chai) and sister (Yap Kiat Fan) for their patience and encouragement that strengthened my vision in completing this thesis. And finally to my loving wife, Chia Sew Yeng, I would not have completed this thesis without your sacrifice and understanding.

YAP KIAT SEN
15th January 2012

# ABSTRACT

The main focus of this work is to develop high conducting solid polymer electrolytes (SPEs). There are three polymer electrolyte systems in this project. Natural rubber (NR) grafted with 30 wt. % poly(methyl methacrylate) (PMMA) and designated as MG30 is used as polymer host and solution cast technique has been employed to produce sample films in this work. X–ray diffraction (XRD) studies have shown that all the samples prepared are amorphous and the morphology of the samples has also been investigated using scanning electron microscopy (SEM). Fourier transform infrared spectroscopy (FTIR) indicates complexation between component materials in the polymer electrolytes based on the changes in peak location and intensity as well as formation of new peaks. The conductivity of pure MG30 film is low, which is about $2.6 \times 10^{-11}$ S cm$^{-1}$ at room temperature. MG30 with 30 wt. % $LiCF_3SO_3$ salt (MG30L) exhibits the highest ambient conductivity of $1.69 \times 10^{-6}$ S cm$^{-1}$ in the single–salt system. Double–salt polymer electrolytes are prepared using different ratios of $LiCF_3SO_3$ and $LiN(CF_3SO_2)_2$ with the total composition maintained at 30 wt. %. The maximum room temperature ionic conductivity is $1.46 \times 10^{-5}$ S cm$^{-1}$ exhibited from the sample MG15L15I consisting of equal ratio of the two salts. The ambient temperature ionic conductivity of plasticized polymer electrolytes increases to a maximum value of $3.65 \times 10^{-4}$ S cm$^{-1}$ with an activation energy of 0.11 eV upon addition of 10 wt. % PEG200 (MG30L–10P) to the MG30L sample. The ionic conductivity of all samples increases with increasing temperature following Arrhenius rule. The dielectric behavior was analyzed using dielectric permittivity and dielectric modulus of the samples. The dielectric constant of pure MG30 is ~ 1.86.

# ABSTRAK

Fokus utama penyelidikan ini ialah menyediakan polimer elektrolit keadaan pepejal (SPE) yang berkonduksian tinggi. Tiga jenis sistem polimer elektrolit disediakan dalam projek ini. 30 % jisim poli(metil metakrilat) cangkukan getah asli yang dikenali sebagai MG30 telah digunakan sebagai perumah untuk sistem elektrolit dan teknik pengacuan larutan telah digunakan untuk menghasilkan sampel filem. Pembelauan sinar–X (XRD) membuktikan bahawa semua sampel adalah berkeadaan amorfos dan pemerhatian morfologi menggunakan mikroskopi imbasan elektron (SEM). Spektroskopi inframerah telah menunjukkan berlakunya pengkompleksan di antara komponen dalam polimer elektrolit berdasarkan perubahan kedudukan panjang gelombang, perubahan dalam keamatan cahaya dan pembentukan puncak baru. Kekonduksian untuk filem MG30 tulen adalah rendah, iaitu lebih kurang $2.6 \times 10^{-11}$ S cm$^{-1}$ pada suhu bilik. MG30 yang telah dicampur dengan 30 % jisim garam $LiCF_3SO_3$ (MG30L) mempunyai kekonduksian yang paling tinggi dalam sistem garam tunggal, iaitu, $1.69 \times 10^{-6}$ S cm$^{-1}$. Sistem dwi garam pula disediakan dengan pelbagai nisbah antara $LiCF_3SO_3$ dan $LiN(CF_3SO_2)_2$ dengan kandungan keseluruhannya kekal pada 30 % jisim di mana kekonduksian maksimum telah diperoleh pada $1.46 \times 10^{-5}$ S cm$^{-1}$ bagi sampel MG15L15I. Nilai maksimum kekonduksian pada suhu bilik dicapai pada $3.65 \times 10^{-4}$ S cm$^{-1}$ dengan tenaga pengaktifan sebanyak 0.11 eV setelah diplastikkan dengan 10 % jisim PEG200 (MG30L–10P). Kekonduksian untuk semua sampel meningkat dengan peningkatan suhu dan mematuhi hukum Arrhenius. Sifat–sifat dielekrik sampel telah dianalisis dengan graf pemalar dielektrik dan modulus dielektrik. Pemalar dielektrik bagi MG30 tulen ialah lebih kurang 1.86.

# TABLE OF CONTENTS

**CONTENT** **Page**

Declaration i

Abstract ii

Abstrak iii

List of Publications iv

Acknowledgement v

Table of Contents vii

List of Figures xi

List of Tables xviii

List of Abbreviations xx

## CHAPTER 1: Introduction to the Present Work

1.1 Background 1

1.2 Objectives of the present work 2

1.3 Scope of the present thesis 3

## CHAPTER 2: Literature Review

2.1 Introduction 5

2.2 Polymer Electrolytes 6

- 2.2.1 Natural rubber (NR) 9
- 2.2.2 Poly(methyl methacrylate) (PMMA) 12
- 2.2.3 Natural rubber (NR) grafted with poly(methyl methacrylate) (PMMA) 14

2.3 Lithium–ion polymer electrolyte 16

2.4 Plasticizer 18

2.5 Models for Ionic Conduction 23

2.5.1 Arrhenius behavior 23

2.5.2 Vogel–Tammann–Fulcher (VTF) behavior 24

2.5.3 Activation Energy ($E_a$) 25

2.6 Summary 26

## Chapter 3: Experimental Method

3.1 Introduction 26

3.2 Samples Preparation 26

3.2.1 Preparation of MG30–$LiCF_3SO_3$ system (Single–salt system) 27

3.2.2 Preparation of MG30–$LiCF_3SO_3$–$LiN(CF_3SO_3)_2$ system (Double–salt system) 28

3.2.3 Preparation of MG30–LiCF3SO3–PEG200 system (Plasticized system) 29

3.3 X–ray diffraction (XRD) 30

3.4 Scanning Electron Microscopy (SEM) 33

3.5 Fourier Transform Infrared (FTIR) Spectroscopy 35

3.6 Electrochemical Impedance Spectroscopy (EIS) 38

3.7 Transference number measurements by Wagner's Polarization Method 42

3.8 Summary 44

## Chapter 4: X–ray Diffraction and Scanning Electron Microscopy Analysis

4.1 Introduction 45

4.2 X–ray diffractogram of MG30–$LiCF_3SO_3$ films 45

4.3 X–ray diffractogram of MG30–$LiCF_3SO_3$–$LiN(CF_3SO_2)_2$ films 49

4.4 X–ray diffractogram of MG30–$LiCF_3SO_3$–PEG200 films 52

4.5 Scanning Electron Microscopy (SEM) 55

    4.5.1 SEM of MG30–$LiCF_3SO_3$ films 55

    4.5.2 SEM of MG30–$LiCF_3SO_3$–$LiN(CF_3SO_2)_2$ films 57

    4.5.3 SEM of MG30–$LiCF_3SO_3$–PEG200 films 58

4.6 Summary 59

## Chapter 5: Infrared Studies of MG30 Complexes

5.1 Introduction 60

5.2 Vibrational studies of MG30–$LiCF_3SO_3$ films 60

5.3 Vibrational studies of MG30–$LICF_3SO_3$–$LiN(CF_3SO_2)_2$ films 77

5.4 Vibrational studies of MG30–$LiCF_3SO_3$–PEG200 films 86

5.5 Summary 100

## Chapter 6: Impedance Spectroscopy Studies of MG30 Complexes

6.1 Introduction 101

6.2 Conductivity studies of MG30–$LiCF_3SO_3$ films 102

    6.2.1 Dielectric studies of MG30–$LiCF_3SO_3$ films 108

6.3 Conductivity studies of MG30–$LiCF_3SO_3$–$LiN(CF_3SO_2)_2$ films 118

    6.3.1 Dielectric studies of MG30–$LiCF_3SO_3$–$LiN(CF_3SO_2)_2$ films 120

6.4 Conductivity studies of MG30–$LiCF_3SO_3$–PEG200 films 127

    6.4.1 Dielectric studies of MG30–$LiCF_3SO_3$– PEG200 films 132

    6.4.2 Transference number measurements 138

6.5 Summary 140

**Chapter 7: Discussion** 141

**Chapter 8: Conclusions and Suggestions for Further Work** 154

**References** 156

# PAPERS PUBLISHED BY AUTHOR IN RELATED AREAS

1. **K.S. Yap**, L.P. Teo, L.N. Sim, S.R. Majid, A.K. Arof, Plasticized polymer electrolytes based on PMMA grafted natural rubber–$LiCF_3SO_3$–PEG200, Materials Research Innovations 15 (2011) 34–38

2. **K.S. Yap**, L.P. Teo, L.N. Sim, S.R. Majid, A.K. Arof, Investigation on dielectric relaxation of PMMA–grafted natural rubber incorporated with $LiCF_3SO_3$, Physica B: Condensed Matter 407 (2012) 2421–2428

# List of Figures

Figure 2.1 Chemical structure of 1,4–*cis*–polyisoprene 9

Figure 2.2 Chemical structure of 50 % epoxidised NR (ENR50) 11

Figure 2.3 Chemical structure of PMMA 12

Figure 2.4 Chemical structure of MG30 (in the structure: R is a free radical) [Ali *et al.*, 2008] 16

Figure 2.5 Chemical structures of (a) lithium triflate and (b) lithium imide 17

Figure 2.6 Chemical structure of PEG200 21

Figure 2.7 Arrhenius plot for the electrolyte with ratio PEO/ENR50 of 70/30 and 80/20 at 20 wt. % LiCF$_3$SO$_3$ [Noor *et al.*, 2010a] 24

Figure 2.8 Temperature dependent ionic conductivity, $E_a$ and $R^2$ value for chitosan–NH$_4$I added with various concentration of PVA [Buraidah and Arof, 2011] 25

Figure 3.1 XRD diffractograms of (a) MG49–6 wt.% TiO$_2$, (b) MG49–30 wt.% LiBF$_4$–2 wt.% TiO$_2$, (c) MG49–30 wt.% LiBF$_4$–6 wt.% TiO$_2$ and (d) MG49–30 wt.% LiBF$_4$–10 wt.% TiO$_2$ [Low *et al.*, 2010b] 31

Figure 3.2 XRD diffractograms of 30/70 MG49–PMMA–LiCIO$_4$ from 2 to 80$^o$ [Su’ait *et al.*, 2009] 32

Figure 3.3 SEM micrographs of (a) MG49–TiO$_2$–LiCIO$_4$, (b) 0 wt. % EC, (c) 10 wt. % EC, (d) 30 wt. % EC and (e) 50 wt. % EC [Low *et al.*, 2010b] 34

Figure 3.4 FTIR spectra in the wavenumber range from 3250 to 650 cm$^{-1}$ of pure MG30. [Ali *et al.*, 2008] 35

Figure 3.5 FTIR spectra in the wavenumber range between (a) 1350 to 1100 cm$^{-1}$ and (b) 1650 to 1800 cm$^{-1}$ for (i) pure LiCF$_3$SO$_3$, (ii) pure MG30, (iii) MG30–35 wt. % LiCF$_3$SO$_3$ and (iv) MG30–45 wt. % LiCF$_3$SO$_3$. [Ali *et al.*, 2008] 37

Figure 3.6 Arrhenius plots of MG49 polymer electrolyte system as a function of PC wt. % at different temperatures [Alias *et al.*, 2005] 40

Figure 3.7 Temperature–dependent conductivity plots of the plasticized and unplasticized GPEs [Ali *et al.*, 2006] 41

Figure 3.8 Cole–Cole plot of MG30–$LiCF_3SO_3$–EC (9:15:76) sample [Ali *et al.*, 2006] 41

Figure 3.9 Cole–Cole plots of GPEs containing various amounts of $LiCF_3SO_3$ [Ali *et al.*, 2006] 42

Figure 3.10 The chronoamperometry of MG30–$LiCF_3SO_3$–EC (9:15:76) under constant voltage of 10 mV [Ali *et al.*, 2006] 43

Figure 4.1 XRD diffractograms of (a) MG0L, (b) MG5L, (c) MG10L, (d) MG15L, (e) MG20L, (f) MG25L, (g) MG30L, (h) MG35L, (i) MG40L, (j) MG45L and (k) $LiCF_3SO_3$ 47

Figure 4.2 Deconvoluted XRD results of (a) MG0L, (b) MG10L (c) MG30L and (d) MG40L 48

Figure 4.3 X–ray diffractograms of (a) MG15L15I, (b) MG20L10I, (c) MG10L20I, (d) MG30L, (e) MG0L and (f) $LiN(CF_3SO_2)_2$ 50

Figure 4.4 Deconvoluted XRD results of (a) MG20L10I, (b) MG15L15I and (c) MG10L20I 51

Figure 4.5 X–ray diffractograms of (a) MG30L–5P, (b) MG30L–7P, (c) MG30L–10P, (d) MG30L–20P, (e) MG30L–30P, (f) pure MG30 and (g) MG30L 53

Figure 4.6 Deconvoluted XRD results of (a) MG30L–7P, (b) MG30L–10P and (c) MG30L–20P 54

Figure 4.7 SEM micrographs at 1000X magnification of (a) MG10L, (b) MG15L, (c) MG20L, (d) MG25L, (e) MG30L, (f) MG35L and (g) MG40L 56

Figure 4.8 SEM micrographs at 1000X magnification of (a) MG10L20I, (b) MG20L10I and (c) MG15L15I 57

Figure 4.9 SEM micrographs at 1000X magnification of (a) MG30L–5P, (b) MG30L–7P, (c) MG30L–10P, (d) MG30L–20P and (e) MG30L–30P 58

Figure 5.1 FTIR spectrum of MG0L sample 61

Figure 5.2 FTIR spectra of (a) $LiCF_3SO_3$ and (b) $LiN(CF_3SO_2)_2$ 63

| | | |
|---|---|---|
| Figure 5.3 | FTIR spectra in the region between 2000 and 650 $cm^{-1}$ of (a) MG0L, (b) MG5L, (c) MG10L, (d) MG15L, (e) MG20L, (f) MG25L, (g) MG30L, (h) MG35L and (i) MG40L | 64 |
| Figure 5.4 | FTIR spectra in the region between 1800 and 1600 $cm^{-1}$ of (a) MG0L, (b) MG5L, (c) MG10L, (d) MG15L, (e) MG20L, (f) MG25L, (g) MG30L, (h) MG35L and (i) MG40L. Image on the right is the enlarged IR spectrum of MG0L | 65 |
| Figure 5.5 | Deconvoluted FTIR spectra in the region between 1800 and 1500 $cm^{-1}$ of (a) MG10L, (b) MG20L, (c) MG30L and (d) MG40L | 67 |
| Figure 5.6 | Deconvoluted FTIR spectra in the region between 1520 and 1400 $cm^{-1}$ of (a) MG10L, (b) MG20L, (c) MG30L and (d) MG40L | 68 |
| Figure 5.7 | FTIR spectra in the region between 1350 and 1210 $cm^{-1}$ of (a) MG0L, (b) MG5L, (c) MG10L, (d) MG15L, (e) MG20L, (f) MG25L, (g) MG30L, (h) MG35L and (i) MG40L | 69 |
| Figure 5.8 | Deconvoluted FTIR spectra in the region between 1350 and 1210 $cm^{-1}$ of (a) MG10L, (b) MG20L, (c) MG30L and (d) MG40L | 70 |
| Figure 5.9 | FTIR spectra in the region between 1220 and 1100 $cm^{-1}$ of (a) MG0L, (b) MG5L, (c) MG10L, (d) MG15L, (e) MG20L, (f) MG25L, (g) MG30L, (h) MG35L and (i) MG40L | 72 |
| Figure 5.10 | FTIR spectra in the region between 1100 and 1000 $cm^{-1}$ of (a) $LiCF_3SO_3$, (b) MG0L, (c) MG5L, (d) MG10L, (e) MG15L, (f) MG20L, (g) MG25L, (h) MG30L, (i) MG35L and (j) MG40L | 73 |
| Figure 5.11 | Deconvoluted FTIR spectra in the region between 1060 and 1000 $cm^{-1}$ of (a) MG10L, (b) MG20L, (c) MG30L and (d) MG40L | 75 |
| Figure 5.12 | Variation of concentration of various states of ions in percentage (%) as a function of $LiCF_3SO_3$ | 75 |
| Figure 5.13 | FTIR spectra in the region between 800 and 700 $cm^{-1}$ of (a) MG0L, (b) MG5L, (c) MG10L, (d) MG15L, (e) MG20L, (f) MG25L, (g) MG30L, (h) MG35L and (i) MG40L | 76 |

Figure 5.14 FTIR spectra in the region between 2000 and 650 cm$^{-1}$ of (a) MG15L15I, (b) MG20L10I and (c) MG10L20I 78

Figure 5.15 FTIR spectra in the region between 1800 and 1600 cm$^{-1}$ of (a) MG15L15I, (b) MG20L10I and (c) MG10L20I 79

Figure 5.16 Deconvoluted FTIR spectra in the region between 1320 and 1200 cm$^{-1}$ of (a) MG15L15I, (b) MG20L10I and (c) MG10L20I 81

Figure 5.17 FTIR spectra in the region between 1210 and 1110 cm$^{-1}$ of (a) MG30L, (b) MG15L15I, (c) MG20L10I and (d) MG10L20I 82

Figure 5.18 FTIR spectra in the region between 1100 and 900 cm$^{-1}$ of (a) MG30L, (b) MG15L15I, (c) MG20L10I and (d) MG10L20I 82

Figure 5.19 Deconvoluted FTIR spectra in the region between 1060 and 980 cm$^{-1}$ of (a) MG20L10I, (b) MG10L20I and (c) MG15L15I 83

Figure 5.20 Variation of concentration of various states of ions in percentage (%) as a function of $LiCF_3SO_3$ 84

Figure 5.21 FTIR spectra in the region between 800 and 700 cm$^{-1}$ of (a) MG30L, (b) MG15L15I, (c) MG20L10I and (d) MG10L20I 85

Figure 5.22 An enlarged IR spectrum of lithium triflate between 780 and 680 cm$^{-1}$ 85

Figure 5.23 FTIR spectrum of PEG200 87

Figure 5.24 FTIR spectra in the region between 2000 and 650 cm$^{-1}$ of (a) MG30L–5P, (b) MG30L–7P, (c) MG30L–10P, (d) MG30L–20P and (e) MG30L–30P 88

Figure 5.25 FTIR spectra in the region between 1800 and 1600 cm$^{-1}$ of (a) MG30L–5P, (b) MG30L–7P, (c) MG30L–10P, (d) MG30L–20P and (e) MG30L–30P 89

Figure 5.26 Deconvoluted FTIR spectra in the region between 1800 and 1500 cm$^{-1}$ of (a) MG30L–5P, (b) MG30L–7P, (c) MG30L–10P, (d) MG30L–20P and (e) MG30L–30P 90

Figure 5.27 FTIR spectra in the region between 1550 and 1350 cm$^{-1}$ of (a) MG30L, (b) MG30L–5P, (c) MG30L–7P, (d) MG30L–10P, (e) MG30L–20P and (f) MG30L–30P 91

| | | |
|---|---|---|
| Figure 5.28 | Deconvoluted FTIR spectra in the region between 1520 and 1400 $cm^{-1}$ of (a) MG30L–5P, (b) MG30L–7P, (c) MG30L–10P, (d) MG30L–20P and (e) MG30L–30P | 92 |
| Figure 5.29 | FTIR spectra in the region between 1350 and 1210 $cm^{-1}$ of (a) MG30L, (b) MG30L–5P, (c) MG30L–7P, (d) MG30L–10P, (e) MG30L–20P and (f) MG30L–30P | 94 |
| Figure 5.30 | FTIR spectra in the region between 1360 and 1200 $cm^{-1}$ of (a) MG30L–5P, (b) MG30L–7P, (c) MG30L–10P, (d) MG30L–20P and (e) MG30L–30P | 95 |
| Figure 5.31 | FTIR spectra in the region between 1100 and 1000 $cm^{-1}$ of (a) MG30L, (b) MG30L–5P, (c) MG30L–7P, (d) MG30L–10P, (e) MG30L–20P and (f) MG30L–30P | 96 |
| Figure 5.32 | Deconvoluted FTIR spectra in the region between 1070 and 1000 $cm^{-1}$ of (a) MG30L–5P, (b) MG30L–7P, (c) MG30L–10P, (d) MG30L–20P and (e) MG30L–30P | 97 |
| Figure 5.33 | Variation of concentration of various states of ions as a function of PEG content | 98 |
| Figure 5.34 | Deconvoluted FTIR spectra in the region between 800 and 700 $cm^{-1}$ of (a) MG30L (b) MG30L–5P, (c) MG30L–7P, (d) MG30L–10P, (e) MG30L–20P and (f) MG30L–30P | 100 |
| Figure 6.1 | Cole–Cole plots of (a) MG10L, (b) MG20L, (c) MG30L and (d) MG40L at 298 K | 103 |
| Figure 6.2 | Cole–Cole plots for MG30L sample at different temperatures (a) 296 K, (b) 298 K, (c) 303 K, (d) 313 K, (e) 323 K and (f) 333 K | 104 |
| Figure 6.3 | Effect of the amount of $LiCF_3SO_3$ on the conductivity of MG30 films at 298 K | 105 |
| Figure 6.4 | Temperature–dependent conductivity plots of (a) MG10L, (b) MG20L, (c) MG30L and (d) MG40L | 106 |
| Figure 6.5 | Log $\sigma$ and activation energy of MG30–$LiCF_3SO_3$ polymer electrolyte system | 107 |
| Figure 6.6 | Variation of (a) $\varepsilon_r$ and (b) $\varepsilon_i$ with frequency of MG30–$LiCF_3SO_3$ samples at 298 K | 110 |
| Figure 6.7 | Variation of $\varepsilon'$ with frequency for various amounts of $LiCF_3SO_3$ in MG30 based polymer electrolytes at 298 K. (Inset shows the enlarged plot at high frequencies) | 111 |

Figure 6.8 Variation of (a) log $\varepsilon_r$ and (b) log $\varepsilon_i$ with log $\omega$ for MG30L sample at different temperatures 113

Figure 6.9 Variation of (a) log $\varepsilon_r$ and (b) log $\varepsilon_i$ with log $\omega$ with various frequencies for MG30L sample at different temperatures 114

Figure 6.10 Variation of tan $\delta$ with frequency for MG30–$LiCF_3SO_3$ polymer electrolytes at 298 K 115

Figure 6.11 Variation of tan $\delta$ with frequency for MG30L sample at different temperatures 116

Figure 6.12 Variation of (a) real ($M'$) and (b) imaginary ($M''$) parts of the electric modulus as a function of log $\omega$ for MG30L sample at different temperatures 117

Figure 6.13 Cole–Cole plots of (a) MG10L20I, (b) MG15L15I and (c) MG20L10I at 298 K 118

Figure 6.14 Conductivity temperature dependence plots of (a) MG30L, (b) MG20L10I, (c) MG10L20I and (d) MG15L15I 119

Figure 6.15 Variation of (a) $\varepsilon_r$ and (b) $\varepsilon_i$ with log $\omega$ of MG30L sample and MG30–$LiCF_3SO_3$–$LiN(CF_3SO_2)_2$ polymer electrolyte system at different temperatures 122

Figure 6.16 Variation of (a) $\varepsilon_r$ and (b) $\varepsilon_i$ with log $\omega$ for MG15L15I sample at different temperatures 123

Figure 6.17 Variation of (a) $\varepsilon_r$ and (b) $\varepsilon_i$ with log $\omega$ for various frequencies for MG15L15I sample at different temperatures 124

Figure 6.18 Variation of tan $\delta$ with frequency for (a) MG20L10I (b) MG15L15I and (c) MG10L20I samples at 298 K 125

Figure 6.19 Variation of tan $\delta$ with frequency for MG15L15I sample at different temperatures 125

Figure 6.20 Variation of (a) real ($M_r$), and (b) imaginary ($M_i$) parts of the electric modulus as a function of log $\omega$ for MG15L15I sample at different temperatures 126

Figure 6.21 Cole–Cole plots of (a) MG30L–5P, (b) MG30L–7P, (c) MG30L–10P, (d) MG30L–20P and (e) MG30L–30P samples at 298 K 128

Figure 6.22 Cole–Cole plots of MG30L–10P polymer electrolyte film at different temperatures 129

| | | |
|---|---|---|
| Figure 6.23 | Plot of log $\sigma$ versus PEG content for (1–$x$) wt. % [70 wt. % MG30–30 wt. % $LiCF_3SO_3$]–$x$ wt. %PEG200 polymer electrolyte system at 298 K | 129 |
| Figure 6.24 | Temperature–dependent conductivity plots of (a) MG30L–5P, (b) MG30L–7P, (c) MG30L–30P, (d) MG30L–20P and (e) MG30L–10P samples | 130 |
| Figure 6.25 | Variation of (a) $\varepsilon_r$ and (b) $\varepsilon_i$ with log $\omega$ for (1–$x$) wt. % [70 wt. % MG30–30 wt. % $LiCF_3SO_3$]–$x$ wt. % PEG200 (where $x$ = 5, 7, 10, 20, 30) polymer electrolyte at different temperatures | 132 |
| Figure 6.26 | Variation of (a) $\varepsilon_r$ and (b) $\varepsilon_i$ with log $\omega$ for MG30L–10P sample at different temperatures | 133 |
| Figure 6.27 | Variation of (a) $\varepsilon_r$ and (b) $\varepsilon_i$ with log $\omega$ for various frequencies for MG30L–10P sample at different temperatures | 135 |
| Figure 6.28 | Variation of tan $\delta$ with frequency for various amounts of PEG200 in 70 wt. % MG30–30 wt. % $LiCF_3SO_3$ polymer electrolytes at 298 K | 136 |
| Figure 6.29 | Variation of tan $\delta$ with frequency for MG30L–10P sample at different temperatures | 136 |
| Figure 6.30 | Variation of (a) real ($M_r$), and (b) imaginary ($M_i$) parts of the electric modulus as a function of log $\omega$ for MG30L–10P sample at different temperatures | 137 |
| Figure 6.31 | The polarization graph obtained using the SS/MG10L–10P/SS cell at 298 K | 139 |
| Figure 6.32 | The polarization graph obtained using the Li/MG30L–10P/Li cell at 298 K | 139 |

# List of Tables

| | | |
|---|---|---|
| Table 2.1 | Examples of modified NR–based polymer electrolytes obtained from literature | 10 |
| Table 2.2 | Examples of PMMA–based polymer electrolytes obtained from literature | 13 |
| Table 2.3 | Examples of MG30 and MG49–based polymer electrolyte systems obtained from literature | 15 |
| Table 2.4 | Examples of lithium salts used in polymer electrolytes | 17 |
| Table 2.5 | Examples of mixed–salt polymer electrolyte systems obtained from literature | 18 |
| Table 2.6 | Examples of plasticizers and its physical properties | 20 |
| Table 2.7 | Examples of polymer electrolytes containing PEG as plasticizer from literature | 22 |
| Table 3.1 | Compositions of MG30–$LiCF_3SO_3$ system | 27 |
| Table 3.2 | Compositions of MG30–$LiCF_3SO_3$–$LiN(CF_3SO_2)_2$ system | 28 |
| Table 3.3 | Compositions of MG30–$LiCF_3SO_3$–PEG200 system | 29 |
| Table 3.4 | FTIR vibrational bands of PMMA–grafted natural rubber (i.e. MG30 and MG49) obtained from literature | 36 |
| Table 4.1 | Degree of crystallinity data of the MG30–$LiCF_3SO_3$ samples | 49 |
| Table 4.2 | Degree of crystallinity data of the MG30–$LiCF_3SO_3$–$LiN(CF_3SO_2)_2$ samples | 52 |
| Table 4.3 | Degree of crystallinity data of the MG30–$LiCF_3SO_3$–PEG200 samples | 54 |
| Table 5.1 | Vibrational assignments of pure MG30 | 61 |
| Table 5.2 | Vibrational assignments of $LiCF_3SO_3$ and $LiN(CF_3SO_2)_2$ | 63 |
| Table 5.3 | Vibrational assignments of PEG200 | 87 |
| Table 6.1 | Conductivity parameters of the MG30–$LiCF_3SO_3$ polymer electrolytes | 108 |

Table 6.2 Conductivity parameters of the MG30–$LiCF_3SO_3$–$LiN(CF_3SO_2)_2$ polymer electrolytes 120

Table 6.3 Conductivity parameters of the MG30–$LiCF_3SO_3$–PEG200 plasticized polymer electrolytes 131

# List of Abbreviations

| | |
|---|---|
| SPEs | Solid polymer electrolytes |
| GPEs | Gel polymer electrolytes |
| CPEs | Composite polymer electrolytes |
| PMMA | Poly(methyl methacrylate) |
| MG30 | Natural rubber grafted with 30 wt. % poly(methyl methacrylate) |
| MG49 | Natural rubber grafted with 49 wt. % poly(methyl methacrylate) |
| EC | Ethylene carbonate |
| PC | Propylene carbonate |
| NR | Natural rubber |
| ENR | Epoxidised natural rubber |
| $LiCF_3SO_3$ | Lithium trifluoromethane sulfonate |
| $LiN(CF_3SO_2)_2$ | Lithium bis(trifluoromethanesulfonimide) |
| $T_\mathrm{g}$ | Glass transition temperature |
| FTIR | Fourier transform infrared |
| XRD | X-ray diffraction |
| SEM | Scanning electron microscopy |
| PEG200 | Poly(ethylene glycol) 200 |
| $\varepsilon$ | Dielectric constant |
| $M$ | Electric modulus |
| $\sigma$ | Conductivity |
| $E_a$ | Activation energy |
| $\tan \delta$ | Loss tangent |
| $\omega$ | Frequency |

| | |
|---|---|
| EIS | Electrochemical impedance spectroscopy |
| THF | Tetrahydrofuran |
| $\tau$ | Relaxation time |

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|---|---|
| Name | YAP KIAT SEN |
| Matrix no | SHC070040 |
| Title of thesis | CHARACTERISTICS OF PMMA-GRAFTED NATURAL RUBBER POLYMER ELECTROLYTES |
| Faculty | FACULTY OF SCIENCE |
| Year | 2012 |