

UNIVERSITI TEKNOLOGI MARA

**EFFECT OF MODIFIED SiO_2
FILLERS ON PROPERTIES OF
PMMA/ENR 50 BLENDS
ELECTROLYTES**

SHARIL FADLI MOHAMAD ZAMRI

Thesis submitted in fulfillment
of the requirement for the degree of
Doctor of Philosophy

Faculty of Applied Sciences

July 2018

ABSTRACT

The polymethyl methacrylate/50 % epoxidized natural rubber (PMMA/ENR 50) blend film was not a homogeneous blend. Therefore in this study, 15 nm (S15) and 20 nm (S20) silicon dioxide (SiO₂) fillers were added to improve the homogeneity and enhance the ionic conductivity of the nanocomposite polymer electrolytes. It was found that the phase separation and the ionic conductivity of the PMMA/ENR 50 blend have been improved when SiO₂ fillers were added. This indicated that SiO₂ fillers played an important role in producing homogenous and improving ionic conductivity nanocomposite polymer electrolytes film. The highest ionic conductivity of $5.26 \times 10^{-6} \text{ Scm}^{-1}$ was obtained when 5 % of S15 was added into lithium tetrafluoroborate (LiBF₄) doped PMMA/ENR 50 (PEL155) blend system. Therefore PEL155 film was suggested as the best film in this study. However, SiO₂ agglomerates can be spotted on the surface of the PEL155 film due to the formation of hydrogen bonding between the silanol (Si-OH) group of the SiO₂ filler with the surrounding moisture. Therefore, S15 was treated with various concentration HCl solutions. It was found that HCl modified S15 (MS15) fillers filled LiBF₄ doped PMMA/ENR 50 electrolyte (PELM155) films exhibit better morphology with minimum filler agglomeration than the PEL155 film. However, their ionic conductivities were lower than the PEL155 film. This indicates that Si-OH group of the SiO₂ filler is crucial for helping dissociation of LiBF₄ salt and needed in forming SiO₂ linkages that provide conducting pathway for the ion transport in the system.

ACKNOWLEDGEMENT

I would like to express my appreciation to all who contribute to this study, especially to my supervisor, Associate Professor Dr. Famiza Abdul Latif, for her guidance, constructive comments, continuous support and advices throughout the duration of this study. I extend my sincere thanks to my co-supervisors, Associate Professor Dr. Ab Malik Marwan Ali for his supervision, support and suggestion.

Sincere thanks are also extended to all Laboratory Assistants in the School of Chemistry and Environment, Universiti Teknologi MARA especially Mr. Mohd Khairul Bin Tajudin, Mr. Dzahir Dzaidanee Bin Nasaruddin, Mr. Hairul Nizam Bin Abdul Razak and Mr. Ahmad Kambali Bin Khalil for their dedication in delivering technical assistance and contribution towards these departments. I also wish to express my appreciation to all staff of the Faculty of Applied Sciences, Universiti Teknologi MARA. My appreciation is further extended to all my senior and junior lab mates in the School of Chemistry and Environment, Faculty of Sciences, and Institute of Science, Universiti Teknologi MARA for their endless support and also providing me with laughter, joy and friendship all the way through.

My deepest affection and gratitude goes to my mother,
my father, my beloved wife, Mrs.
Noor Syakkila Binti Zulkifli, my children, Sofea Batrisyia Binti Sharil Fadli, Shamil Bin Iman Sharil Fadli, Shamir Haykal Bin Sharil Fadli and Safea Ayuni Binti Sharil Fadli for their continuous doa, understanding and moral support throughout the period of my study.

Last but not least, Special thanks to Universiti Teknologi MARA and Ministry of Science, Technology and Innovation for the financial and technical supports under FRGS and RAGS grant.

TABLE OF CONTENTS

	Page
CONFIRMATION BY PANEL OF EXAMINERS	ii
AUTHOR'S DECLARATION	iii
ABSTRACT	iv
ACKNOWLEDGEMENT	v
TABLE OF CONTENTS	vi
LIST OF TABLES	xi
LIST OF FIGURES	xiii
LIST OF SYMBOLS	xix
LIST OF ABBREVIATIONS	xxii
CHAPTER ONE: INTRODUCTION	1
1.1 Background of study	1
1.2 Problem statements	3
1.3 Objectives	4
1.4 Scope of study	4
1.4.1 Selection of materials	4
1.4.2 Selection of characterization method	5
1.5 Significance of the study	6
1.6 Novelty of the study	7
CHAPTER TWO: LITERATURE REVIEW	8
2.1 Polymer electrolytes	8
2.1.1 What is a polymer electrolyte?	8
2.1.2 History of polymer electrolytes	9
2.1.3 Selection of polymer host	9
2.1.4 Type of polymer electrolytes	10
2.1.5 Ionic conductivity and mechanism of ionic transport in polymer electrolytes	12

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND OF STUDIES

Today, most human activities such as working, communicating and traveling involved the use of electronic devices such as cell phones, laptops, cameras and global positioning systems (GPSs). These technologies produced smaller and portable devices hence it needs a smaller and lightweight battery that can power these electronic devices. Therefore, the performance of the battery needs to be improved so that it may last longer and stable at wide temperature range, can be recharged at reasonable rate, non-toxic and low in cost (Goodenough and Kim, 2011). There are several types of rechargeable batteries that has been developed such as Li^+ ion battery (Wu et al., 2017), Mg^{2+} ion battery (Wang et al., 2017) and Na^+ ion battery (Guerfi et al., 2016). Amongst them Li^+ ion battery has been extensively researched due to stable cycling, high energy density, high voltage, and environmentally-friendly (Wu et al., 2017).

A Li^+ ion battery consists of anode, cathode and electrolyte that are assembled together to form a battery system (Zhou et al., 2010). The performance of a battery was determined by the type of materials utilized. Thus, the development of new materials for battery components is crucial in order to obtain desired battery performances (Scrosati & Garche, 2010, Goodenough & Kim, 2010). Most development of battery focusses on obtaining an electrolyte material that has high energy density, good charge/discharge cyclic stability as well as high safety (Wang et al., 2014). Polymeric materials has been extensively chosen in developing electrolyte for Li^+ ion battery because it is able to give reasonable conductivity, high mechanical strength and stable at a wide range of temperature (Krejza et al., 2008). The idea of using polymer as electrolyte has been started in 1970s by Feton and co-workers (1973) and followed by Wright (Wright, 1975, Wright, 1998). However, its potential as electrolyte material in electrochemical devices has only been realized by Armand et al., (1979) in which a non-conducting polymer of poly(ethyleneoxide) (PEO) was able to conduct electricity when inorganic salt (Wright, 1998) was added into the polymer matrix. This new class of polymer is called polymer electrolytes.