UNIVERSITI TEKNOLOGI MARA

PREPARATION AND CHARACTERIZATION OF POLY (METHYL METHACRYLATE) / IRRADIATED - 50% EPOXIDIZED NATURAL RUBBER BASED SOLID ELECTROLYTES

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Candidate's Declaration

I declare that the work in this thesis was carried out in accordance with the regulations of University Teknologi MARA. It is original and is the result of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any other degree or qualification.

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ABSTRACT

Previously poly (methyl methacrylate) has exhibited high ionic conductivity when it was fabricated in gel form. However, this gel electrolyte exhibited poor mechanical stability. Therefore, in order to obtain a better mechanical stability of PMMA based electrolyte, it needs to be prepared in a film form. Unfortunately, this PMMA film is brittle. Therefore, in this study it was blended with 50% epoxidized natural rubber that has soft elastomeric, good elasticity and adhesion properties. Due to the nature of the rubber to form inter-chain cross-linking that may limits the segmental motion of the polymer electrolyte system, therefore, it was irradiated under UV light at various irradiation time to reduce the number of inter-chain cross-linking in the rubber system. All the PMMA / iENR 50 films were prepared by solvent casting technique and the films were then characterized using optical polarizing microscopy, differential scanning calorimetry (DSC), thermo-gravimetric analysis / differential thermo-gravimetric analysis (TGA/DTA), Fourier Transform Infrared (FTIR) and impedance spectroscopy. From the DSC analysis, it was found that the T_g of un-irradiated ENR 50 was reduced from -25°C to -26°C when it was irradiated for 30 seconds indicating that it has the highest chain flexibility as a result of breaking of the inter-chain cross-linking. Therefore, it can be concluded that it requires only 30 seconds of UV irradiation to heal the inter-chain cross-linking in the ENR 50 system. The reduction of the number of inter-chain cross-linking has been confirmed by the reduction of the intensity of the OH band at 3440-3424 cm^{-1} followed by the increased in the intensity of the epoxy ring at 1255 cm^{-1}. When this 30iENR 50 was blended with PMMA, it produced the most flexible freestanding film as compared to un-irradiated and other irradiated ENR 50 systems. Furthermore, this PMMA / 30iENR 50 exhibited the highest conductivity of 1.03 X 10^{-4} S/cm due to the flexibility of the polymer chain and the formation of a less viscous phase that favor the migration of lithium ion in the blend matrix. The addition of PC plasticizer further enhanced the conductivity of the PMMA / 30iENR 50 / $LiCF_3SO_3$ electrolyte to 1.16 X 10^{-3} S/cm. The ionic conduction of the doped PMMA / 30iENR 50 system was found to obey the Arrhenius behaviour in which the migration of ions was thermally assisted. Interestingly, there were two activation energies (E_a) were observed from the doped PMMA / 30iENR 50 electrolytes in which the E_{a2} at higher temperature was less than E_{a1} observed at lower temperature due to the change of the phase from crystalline to an amorphous phase at 70°C. This was confirmed from the DSC thermogram of the blend system. However, for the plasticized PMMA / 30iENR 50/ $LiCF_3SO_3$ electrolyte, the ionic conduction was due to the segmental motion of the polymer indicating that the presence of PC enhanced the mobility of the polymer.

TABLE OF CONTENTS

CHAPTER 1

INTRODUCTION

Conventional liquid electrolytes are facing problems such as leakage of corrosive, flammable and toxic liquids or gaseous which are to date remain unsolved. Therefore, these liquid based electrolytes should be replaced by solid based electrolyte to overcome these problems.

Solid electrolytes are a class of solid substances, which can conduct electrical current by ionic motion. These materials can be divided into three categories: crystalline compounds such as 12-phosphotungstic acid (PWA) and the ionic liquid [1-butyl-3-methyl imidazole] [bis-(fluoromethanesulfonyl) amide] (BMIM) [TFSI] (Kim *et al.*,2008), glasses such as AgI-Ag_2O-B_2O_3/Al_2O_3 (Foltyn *et al.*, 2007) and polymers such as polyethylene-b-poly(ethylene oxide) (PE-b-PEO) / lithium per chlorate ($LiClO_4$) (Guilherme *et al.*, 2007). Among these, the most popular type of solid electrolyte is the polymer electrolyte. This is due to their unique properties (Chandra, 1994) which include:

a) Ease of preparation in thin film form.
b) Ability to accommodate a wide range of doping salts composition.
c) Provide good electrode-electrolyte contact.
d) Exhibit high ambient ionic conductivity.