

**UNIVERSITI TEKNOLOGI MARA**

**EFFECT OF TiO<sub>2</sub> FILLER ON THE  
STRUCTURAL, ELECTRICAL AND  
TENSILE PROPERTIES OF  
HEXANOYL CHITOSAN-  
POLYSTYRENE BLEND POLYMER  
ELECTROLYTE**

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## ABSTRACT

The insolubility of chitosan in aprotic solvents is inadequate to meet the requirements to be used as an electrolyte material in lithium-based electrochemical devices. Acyl modification of chitosan helped to improve its solubility in aprotic solvent. However, hexanoyl chitosan-based polymer electrolytes are of poor mechanical property. A convenient method to improve the mechanical property of hexanoyl chitosan is to blend it with a polymer with good mechanical strength. In this respect, polystyrene was chosen as a blending partner for hexanoyl chitosan. In this work, blends of hexanoyl chitosan and polystyrene are used as the polymer host,  $\text{LiCF}_3\text{SO}_3$  and  $\text{TiO}_2$  are employed as the doping salt and filler, respectively. Surface treatment of  $\text{TiO}_2$  is done by immersing filler particle in 2 and 4% sulphuric acid ( $\text{H}_2\text{SO}_4$ ) aqueous solutions. Untreated, 2 and 4%  $\text{H}_2\text{SO}_4$ -treated  $\text{TiO}_2$  were referred as neutral, weakly acidic and acidic  $\text{TiO}_2$  respectively. X-Ray diffraction (XRD), Fourier Transform Infrared (FTIR), tensile test, viscometry and impedance spectroscopy (EIS) are used to characterize the prepared samples. Viscometric analysis showed that hexanoyl chitosan and polystyrene are immiscible. Tensile test revealed that blending hexanoyl chitosan with polystyrene increased its mechanical properties, and greater improvement is found with addition of  $\text{TiO}_2$  fillers. XRD results showed that, polystyrene disrupted the crystalline nature of hexanoyl chitosan. Addition of  $\text{TiO}_2$  further reduced the crystalline fraction of hexanoyl chitosan/polystyrene based electrolytes. FTIR studies showed that there is no interaction between polystyrene and  $\text{LiCF}_3\text{SO}_3$ . Hexanoyl chitosan interacted with  $\text{LiCF}_3\text{SO}_3$  from the shift of  $\text{C}=\text{O}$  of  $\text{N}(\text{COR})_2$  and  $\text{OCOR}$  bands to lower wavenumbers. There is also no interaction between polystyrene and hexanoyl chitosan. Interaction between  $\text{TiO}_2$  and  $\text{LiCF}_3\text{SO}_3$  is indicated by the shift in wavenumber, changes in intensity and shape of peaks of  $\text{LiCF}_3\text{SO}_3$ .  $\text{TiO}_2$  did not interact with hexanoyl chitosan nor polystyrene. The conductivity performance of hexanoyl chitosan/polystyrene- $\text{LiCF}_3\text{SO}_3$  polymer electrolytes varied in the order: acidic < weakly acidic <  $\text{TiO}_2$  free < neutral  $\text{TiO}_2$ . A model based on the interaction between Lewis acid-base sites of  $\text{TiO}_2$  with ionic species of  $\text{LiCF}_3\text{SO}_3$  has been proposed to understand the conductivity mechanism brought about by the different types of fillers. The conductivity enhancement by neutral  $\text{TiO}_2$  is attributed to the increase in the mobility of  $\text{Li}^+$  cations. Acidic  $\text{TiO}_2$  decreased the conductivity by decreasing the anionic contribution. The conductivity variation with filler content is discussed on the basis of the number of free ions. Conductivity of the prepared electrolyte system is also studied as a function of temperature, ranging from 273 to 333 K. The conductivity was found to increase with increasing temperature.

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# CHAPTER ONE

## INTRODUCTION

### 1.1 RESEARCH BACKGROUND

Polymer based electrolytes are increasingly popular in advanced application especially in electrochemical system as they offer good mechanical properties, fair filmability, shape and design flexibility and good contact with electrode materials. Generally, polymer electrolytes could be classified into three categories: solid polymer electrolytes (SPEs), gel polymer electrolytes (GPEs) and composite polymer electrolytes (CPEs). SPE has attracted considerable attention in view of its potential application in variety of electrochemical devices, especially in rechargeable lithium polymer batteries due to their high ionic conductivity, high energy density, leak proof and easy fabrication (Baskaran et al., 2004).

SPE is defined as a thin film consists of alkali metal salts dissolved in an appropriate polymer matrix, which enable ionic conduction at room temperature (Gray, 1997). The ionic conduction is due to the mobile ions as a result of salt dissociation. Poly(ethylene oxide) (PEO) was the earliest and the most widely studied polymer electrolyte system due to its system ability to effectively coordinate with the salt cations and to form homogenous solutions (Fenton et al.,1973). However, due to the high degree of crystallinity of PEO, complexes of PEO-salt were poor ionic conductors at room temperature ( $\sigma \approx 10^{-7}$  to  $10^{-8}$  S cm<sup>-1</sup>) (Liu et al., 2003). The ionic conductivity can be improved to between  $10^{-6}$  and  $10^{-4}$  S cm<sup>-1</sup> with addition of various liquid plasticizers. A major drawback of these plasticized polymer-salt complexes mechanical properties are often sacrifices.

Another promising way to improve both the mechanical and conductivity properties of polymer electrolyte is the incorporation of inorganic fillers such as TiO<sub>2</sub>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> to form a kind of composite polymer electrolyte (CPE). Various CPE systems have been reported in the literature. The role played by the fillers as the conductivity enhancer, however, is still unclear. Some researchers suggested that the conductivity