

UNIVERSITI TEKNOLOGI MARA

**MISCIBILITY STUDY OF
POLY(ETHYLENE OXIDE)/
POLYACRYLATES BLENDS USING
THERMAL, MORPHOLOGY, MELT
RHEOLOGICAL AND
CONDUCTIVITIES PROPERTIES
OF THE BLENDS WITH LITHIUM
PERCHLORATE**

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ABSTRACT

Miscibility on binary blend system of the high molar mass of poly(ethylene oxide) (PEO) ($M_n = 300,000 \text{ g mol}^{-1}$) with polyacrylates such as poly(methyl acrylate) (PMA) ($M_w = 40,000 \text{ g mol}^{-1}$) and poly(*n*-butyl methacrylate) (PnBMA) ($M_w = 337,000 \text{ g mol}^{-1}$) were studied. The thin films of the samples were prepared via the solution casting method with various mass percent ($m/m \%$) compositions ranging from 0/100 to 100/0. The investigation of the miscibility was by thermal characterization using differential scanning calorimeter (DSC). The miscibility of PEO/PMA blends is confirmed through the presence of single and composition-dependent glass transition temperature, T_g which follows the Fox equation and the reduced apparent melting temperature, T_m of PEO (from $66 \text{ }^\circ\text{C}$ to $53 \text{ }^\circ\text{C}$) throughout the blend compositions. On the other hand, PEO and PnBMA are immiscible for entire blend compositions where the quantities T_g of PEO in the blends remain constant with T_g of neat PEO which is $-53 \text{ }^\circ\text{C}$ while quantities change of heat capacity, ΔC_p of PEO show increment with the increasing mass fraction of PEO, W_{PEO} which marks the constancy of quantity ΔC_p of PEO in the blends. Also, the insignificant variation of T_m of PEO ($\sim 66 \text{ }^\circ\text{C}$) and the constancy of the crystallinity, X^* of PEO in the blends imply that these blends are immiscible agreed with the results of T_g and ΔC_p . The optical micrographs taken using an optical microscope at the molten state further corroborate the homogeneity of PEO and PMA phases with the Han plots from the melt rheological studied at $T = 80 \text{ }^\circ\text{C}$ superimpose to one another and the slopes do not vary significantly. In contrast, the heterogeneity is confirmed where matrix-droplet and co-continuous structures can be observed. Meanwhile, the Han plots do not superimpose and the slopes vary dependently on the blends' compositions which implies the immiscibility between PEO and PnBMA. From the correlation of the thermal, morphology and melt-rheological behaviour of miscible PEO/PMA and immiscible PEO/PnBMA blends presented, we may conclude that the behaviour of the binary systems of the polymers may vary depending especially on their molar mass and molecular structure. The entanglement of the polymers (especially for high molar mass) may affect the flow behaviour especially when the systems are in the molten state. These correlations follow a simple model like Flory-Huggins theory which offers new insight into the miscibility of polymer blends with high molar mass. This understanding is crucial for determining the optimal compositions prior to incorporating additional components, such as salt, in the preparation of solid polymer electrolytes (SPE) for various applications. Additionally, the selected blends of PEO/PnBMA (80/20, 60/40 and 10/90) blends compositions with the addition of lithium perchlorate, LiClO_4 (with salt concentration, $W_s = 0.00099$ to 0.107) were studied. The studies incorporated with salts were also compared with a few blend systems from the literatures. PEO/PnBMA blends studied exhibiting the liquid-liquid phase separation upon the addition of salt with the constancy of quantity T_g of neat polymers (at $W_{\text{PEO}} = 0$). It can be concluded that upon the addition of salt, the immiscibility of the systems still could not improve. Impedance spectroscopy (IS) studies show that the ionic conductivities (σ_{DC}) of the polymer blends at room temperature slightly increase with increasing PEO with the order of magnitude of $10^{-11} - 10^{-10} \text{ S cm}^{-1}$. However, the addition of salt into the PEO/PnBMA blends system does not improve the σ_{DC} .

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CHAPTER 1

INTRODUCTION

1.1 Research Background

The demand for high performance (*e.g.* small, lightweight, high-energy density *etc*) electronic devices such as cell phones, laptops, tablets *etc* is getting higher nowadays. Hence, the demand for rechargeable power sources is now focusing on solvent-free polymer electrolytes, which have been attaining great research attention both academically and industrially over the last two decades (Abd Karim et al., 2013; Halim et al., 2017; Harun, Chan, & Winie, 2017; Rajendran et al., 2002; Sun et al., 2017; Xiong et al., 2001; Yu et al., 2017).

Solid polymer electrolytes (SPEs) (the solvent-free polymer electrolytes) based on poly(ethylene oxide) (PEO) as a polymer host have been extensively studied (Acosta & Morales, 1996; Armand, 1986; Harun, Chan, & Winie, 2017; Rocco et al., 2002, 2004; Silvestre et al., 1987), due to its high solvating capability of wide variety of metallic salts such as lithium sulfate (Li_2SO_4) (Manjunatha et al., 2014; Ramesh et al., 2008), lithium iodide (LiI) (Dai et al., 1998; Rao & Suvarna, 2016), lithium triflate (LiCF_3SO_3) (Fan et al., 2008; Karmakar & Ghosh, 2010; Ramesh et al., 2008), lithium bis(fluorosulfonyl)imide (LiFSI) (Gracia et al., 2018; H. Zhang et al., 2014), lithium perchlorate (LiClO_4) (Cheng et al., 2017; Fullerton-Shirey & Maranas, 2010; X. Zhang et al., 2018) and lithium tetrafluoroborate (LiBF_4) (Fahmi et al., 2012; Voigt & Van Wüllen, 2014). However, the binary systems of PEO and salt display low conductivity ($\sigma_{\text{DC}} \sim 10^{-6} - 10^{-8} \text{ S cm}^{-1}$) (Abd Karim et al., 2013; Chan & Kammer, 2008; Cimmino et al., 1988; Sim et al., 2009) and show slightly higher conductivity ($\sigma_{\text{DC}} \sim 10^{-4} \text{ S cm}^{-1}$) above its melting temperature at around 65 °C (Armand, 1986; Wang et al., 2003) and hence, they are not suitable for the commercial application at ambient temperature. This is due to the high crystallinity of PEO (up to 70 %) for high molar-mass SPEs (Fan et al., 2008; Halim et al., 2017; Harun, Chan, & Winie, 2017; Karim et al., 2015; Xiong et al., 2001). Thus, various approaches have been made to enhance to conductivity of SPEs such as addition of plasticizers (Freitag et al., 2018; Qian et al., 2002; Walker & Salomon, 1993) and fillers (Alloin et al., 2010; Bloise et al., 2001; Croce et al., 1998;