UNIVERSITI TEKNOLOGI MARA

MISCIBILITY, CONDUCTIVITY AND INTERMOLECULAR INTERACTION STUDIES OF POLY(ETHYLENE OXIDE) AND POLY(METHYL METHACRYLATE) BLEND BASED NANOCOMPOSITE POLYMER ELECTROLYTES

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ABSTRACT

The addition of the third component into the polymer-salt system such as nanofiller has been extensively studied by researchers to increase the amorphous region of the polymer electrolyte system, thus improving the ion movement in the polymer chain. In most studies, the range of ionic conductivity of nanocomposite polymer electrolyte (NCPEs) can be up to ~10^{-4} S cm^{-1} and high σ_{DC} is recommended for use in applications. The success of the solid polymer electrolyte (SPEs) and NCPEs could be applied to energy storage device, electronic vehicle and capacitor for the future generation. However, the effective role of the nanofiller in promoting ion transport is not yet well understood. Therefore, this research is an effort to govern the understanding of the dispersion and effective role of the nanofiller of the most studied blend, Poly(ethylene oxide) (PEO)/Poly(methyl methacrylate) (PMMA) with lithium perchlorate ($LiClO_4$). Differential scanning calorimetry (DSC) was used to study the thermal behaviour of the SPEs and NCPEs. A single and composition-dependent glass transition temperature (T_g) is observe for all blend compositions with increasing content of PMMA in the blend and it follow closely to that Gordon-Taylor equation. Addition of TiO_2 does not give influence to the T_gs of PEO due to the absence of interaction between PEO and TiO_2, but significantly raises the T_gs of PMMA. Studies on crystallinity (X^*) shows that addition of PMMA and also TiO_2 cause distortion on the PEO spherulites shape. The reduction of dark regions in the inter-spherulite region indicates TiO_2 has weaken the linkage of O-Li through the Lewis acid-base interaction. Close inspection of the SEM micrographs observes that at low TiO_2 content, the nanofiller are homogeneously disperse with no nanoparticle aggregation in the salt-free and salt-added neat PEO as well as the PEO/PMMA blend matrix. Addition of $LiClO_4$ enhances the conductivity of PEO and it records a maximum σ_{DC} value of 1.38×10^{-6} S cm^{-1} at $Y_S = 0.10$, then follow by PEO/PMMA 75/25 which exhibit σ_{DC} value of 7.00×10^{-7} S cm^{-1} at the same amount of Y_S as PEO. In the presence of TiO_2, the σ_{DC} values of the salt-free neat PEO and neat PMMA remain unchanged with ascending nanofiller content. However, the σ_{DC} values of the PEO/PMMA 75/25 blend decreases by one order of magnitude. PEO/PMMA 75/25 at $Y_S = 0.10$ shows the shortest relaxation time (τ_{max}) among the blend composition. Overall, PEO/PMMA 75/25 blend system has the best ε', ε'', M' and M'' values which are very close to the respective values of PEO system, thus accounts for its best ion conductivity among the rest of the blend systems investigated. The intermolecular interaction studies by FTIR have shown that addition of $LiClO_4$ cause the shifting of characterized peak in PEO, PMMA and its blend, however addition of TiO_2 has proved that the nanofiller is more active to the salt-added PEO/PMMA 75/25 system as compared to the parent polymers. The observation of crystal structure under XRD have shown that $LiClO_4$ and TiO_2 give effect on the crystal structure of PEO and PEO/PMMA blend, supporting the observation done by other instruments studied in this research.

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CHAPTER ONE
INTRODUCTION

1.1 BACKGROUND OF STUDY

Polymer came from the Greek words *poly* (many) and *meros* (chain). It is formed by connecting many monomers by covalent bonds. Polymer can be divided into two classification based on their origins of natural or man-made resources. Protein is one of the examples of natural polymer that is in every organism on earth. Natural rubber (NR) is another example of natural polymer which has many applications both domestically and industrially since it was first discovered by DuPont.

After World War II in the 20th century, major leaps in technology resulted in a great demand for materials in the construction, engineering, automobile as well as domestic sectors have exhausted natural resources for materials. The dire need to replace conventional natural materials by synthetic materials to cater for the fast pace of industrial development and to meet the demand for cheaper yet good quality materials give rise to the era of plastics and polymeric materials. In the 1950s, the production of synthetic polymers flourished rapidly and became the most important industry in the world (Utracki, 2002).

Polymers can be categorised into crystalline and amorphous polymer based on the alignment of the macromolecular chains in the polymer matrix. Crystalline polymers are more correctly termed as semicrystalline as their measured densities differ from those obtained for perfect materials. Figure 1.1 shows the lamellae structure of crystalline polymer. The lamellae or platelet-like crystallites are the major structural units in the semicrystalline polymer. Figure 1.2 shows random chain structure of an amorphous polymers of commercial importance include polymers which are glassy or rubbery at room temperature (Sawyer and Grubb, 1996). Figure 1.3 depicts "Fringe micelle model" which represent the presence of crystalline and amorphous regions in a semicrystalline polymer.