

UNIVERSITI TEKNOLOGI MARA

**THERMAL PROPERTIES AND
DIELECTRIC RESPONSE OF
POLY(ETHYLENE OXIDE) /
POLY(METHYL ACRYLATE)
BLENDS WITH ADDITION OF SALT
AND NANOFILLER**

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ABSTRACT

A series of systematic study comprises elucidation on phase behaviour, dielectric relaxation, and other important properties on semi-crystalline/amorphous poly(ethylene oxide)/poly(methyl acrylate) PEO/PMA blends after addition of lithium perchlorate (LiClO_4) and titanium dioxide (TiO_2) were done for different compositions. The manipulated variables here are the mass fraction of PEO, Li-salt and TiO_2 -nanofiller. The study was allocated into a series of systems for systematic understanding on the properties of each system *i.e.*, polymer-salt, PEO/PMA polymer-blend, PEO/PMA polymer-blend solid polymer electrolyte and PEO/PMA polymer-blend composite polymer electrolyte. The samples were prepared through solution casting technique to fabricate the solid solutions with appreciable energy density and leakage-free electrolytes for the application of energy storage. Each property of each system was investigated from the phenomenological point of view complemented with theoretical analyses for elucidation of the overall properties. The first section of the study elucidates on the thermal and dielectric properties of several polymer-salt systems examined by differential scanning calorimetry (DSC) and electrochemical impedance spectroscopy (EIS), respectively. Findings show the variation in glass transition temperature (T_g) with increasing salt content. Dielectric responses of PEO and PMA with salt at 25 °C reveal that PEO is electrically conductive even at low mass fraction of salt unlike PMA, where it became slightly conductive only with high salt content. PEO and PMA were opted for the next section of the study due to the desirable properties for polymer blending. In the second section, the blend stability, miscibility and intermolecular interaction of PEO/PMA blends were explored. PEO has a better thermal stability than PMA based on the thermogravimetric analysis (TGA), which is also true for blends with PEO in excess. DSC analysis suggests the existence of a single and composition-dependent T_g for the blends with 10 wt.% interval difference indicates the miscibility of the PEO/PMA blends. Fourier-transform infrared (FTIR) spectroscopy does not suggest the intermolecular interaction between PEO and PMA in the blends. This miscibility of PEO and PMA may be due to the entropic effect instead of enthalpic effect since PEO and PMA only display weak *van der Waals* interactions in blends. Next, the PEO/PMA blends with addition of LiClO_4 were studied. The miscibility of the PEO/PMA blends after addition of salt relied on the content of PEO is suggested. The blends are only miscible when PEO is in excess ($> \sim 60$ wt.%) by displaying a single and compositional-dependant T_g with salt. Results of T_g using DSC, molecular interaction from FTIR and dielectric response from EIS suggest that the charged entities of LiClO_4 coordinate with ether oxygen of PEO instead of carbonyl oxygen of PMA for blends with PEO in excess (*e.g.*, T_g of PEO_{80} increases from -31°C to -26°C for $W_s = 0.0196$ to 0.091). Hence, the percolation pathway for these electrolytes may be lying in the amorphous region of the PEO phase. The effect of addition of TiO_2 on the phase behaviour, conductivity and intermolecular interaction of PEO/PMA blends were elucidated in the last section of the study. Findings suggest that salt preferably dissolves in PEO phase as compared to PMA phase while TiO_2 does not coordinate well either to PEO or PMA phase in the presence of salt since the T_g s of PEO and PMA after addition of TiO_2 show insignificant difference as compared to the T_g of the pure polymers. These outcomes elucidates the properties of the polymers may be altered based on the interactions between the constituents in the mixture.

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