In this study, immiscible blends of poly(ethylene oxide) (PEO) and epoxidized natural rubber with 50 mol% epoxide content (ENR-50) added with lithium perchlorate (LiClO4) and nano-sized titanium dioxide (TiO2) were studied. To have a systematic comparison, a series of systems of PEO/LiClO4, PEO/TiO2, PEO/LiClO4/TiO2, ENR-50/LiClO4, ENR-50/TiO2, ENR-50/LiClO4/TiO2, PEO/ENR-50, PEO/ENR-50/LiClO4 and PEO/ENR-50/LiClO4/TiO2 were prepared via solution casting method. The thermal properties, conductivity, intermolecular interaction, morphologies, crystalline structures and rheological behavior were studied accordingly with greater emphasis on the relationship between thermal properties and conductivity behaviour. From impedance spectroscopy analysis, the ionic conductivity at room temperature was found in the order of PEO/LiClO4 > PEO/ENR-50/LiClO4 > PEO/ENR-50/LiClO4/TiO2 > ENR-50/LiClO4 > ENR-50/LiClO4/TiO2 at constant salt concentration.

The highest conductivity achieved is ~10^-7 S cm^-1 for PEO/LiClO4 system. From differential scanning calorimetry (DSC) analysis, the trend of glass transition temperature(s) which represents the segmental motion of polymer(s) is different for each particular system. The glass transition temperature shows that most of the LiClO4 salt dissolves in the amorphous phase of PEO rather than ENR-50 in the blend. The role of TiO2 filler contributing to the ionic conductivity of PEO-blend CPEs is still ambiguous. This underlines the importance of polymer(s)-salt-filler interaction, polymer(s) segmental motion, morphologies, location of salt, location of filler etc in understanding conductivity percolation path of immiscible PEO/ENR-50 blend-composite polymer electrolytes.