CHAPTER - 5

CONCLUSION AND FUTURE SCOPE OF THE WORK
5.1 Conclusion

Hydroxyl propyl methyl cellulose (HPMC) based polymer electrolyte systems were prepared by solution cast technique. Different inorganic salts like, sodium iodide (NaI), cadmium chloride (CdCl2) and ceric ammonium nitrate (NH4)2Ce(NO3)6 (CAN) are used as doping salts in different ratios. The structural, thermal and ionic conductivity behavior of these polymer electrolyte systems upon gamma irradiation with different doses of 20, 60 and 100 kGy was studied. Several experimental techniques like XRD, SEM, FTIR, DSC and dc electrical conductivity were carried out to characterize these polymer electrolyte films before and after gamma irradiation.

The complexation of the dopant salt with the host polymer in all polymer electrolyte systems, before and after irradiation is confirmed by XRD studies. XRD study showed the percentage of crystallinity decreases with the increasing concentration of salt and gamma dose in all complexed systems. Hence the addition of inorganic salt causes a decrease in the degree of crystallinity and a simultaneous increase in the amorphousity. For pure HPMC, a slight increase in crystallinity is observed at low radiation dose (20 kGy), whereas crystallinity decreases at higher doses (60, 100 kGy). This may be due to the cross linking of the polymer chain or by the formation of the single or multiple helices, which induces more crystalline region in the polymer samples. In all polymer electrolyte systems, the presence of dopant salt prevent polymer chain reorganization resulting in decreased crystallinity compared to pure HPMC before and after gamma irradiation. Hence it may be mentioned that during irradiation, the energy deposited in the polymer causes chain scission or produce radicals which subsequently decay or cross-link with neighboring radicals, i.e. both chain scission and cross-linking occur during irradiation.

SEM is used to investigate the morphology of these samples. By analyzing the SEM images, the higher porosity revealed the improved ionic migration in all the polymer electrolyte systems. SEM of pure HPMC films exhibits no features attributable to any crystalline morphology, so the semi crystallinity of HPMC is likely to be submicroscopic in nature. The increase in the degree of roughness and dense structure with the increasing concentration of doping salt indicates the segregation of the dopant in that host polymer matrix. The two phase microstructure in the SEM image reflects the phase separation at different concentration of the doping salt. Therefore morphological studies clearly indicate the phase segregation phenomenon
in these complexed polymer electrolyte systems. It is observed that during irradiation, pure HPMC shows porous structure with well dispersed pores for low doses at 20 kGy. On the other hand, at 60 kGy, the porous structure is disrupted possibly due to recrystallization of the polymer. Whereas HPMC and salt complexed systems shows loosely bound porous structures due to irradiation effects at higher doses (60, 100 kGy). This may be due to the rapid penetration of ions into the polymer matrix at higher doses. Considerable damage in the polymeric structure was observed during irradiation, which is also responsible for decrease in the crystallinity of the material.

Fourier Transform infrared (FTIR) spectroscopy indicated the complexation of the materials in the polymer electrolytes based on the changes in peak shifting, intensity, shape and formation / disappearance of the new peaks. DSC studies inferred the improved thermal properties of samples. The DSC results revealed that the presence of dopant salt in the polymer matrix increases the melting temperature in un-irradiated samples. For pure HPMC, after irradiation (20, 60 and 100 kGy), the melting temperature decreases. However it is observed that the heat of fusion ($\Delta H_f$) is high for pure HPMC samples when compared with the salt complexed films, before and after irradiation suggesting the relative percentage of crystallinity also reduces in all other polymer electrolyte systems. These results are also in good agreement with the percentage of crystallinity obtained from XRD studies.

The temperature dependent ionic conductivities of all polymer electrolyte samples increased with temperature. The temperature dependence of electrical conductivity ($\sigma$) follows Arrhenius behavior and thus further indicated the ion hopping mechanism. The increase in conductivity with the increasing temperature, salt concentration and gamma radiation dose is attributed to the decrease in the degree of crystallinity and the simultaneous increase in amorphousity. This is because the effect of ionizing gamma irradiation on polymer is to rupture chemical bonds and create energetic free electrons, ions, and radicals, which are able to migrate through the network, leading to a change in electrical conductivity. Also the hopping mechanism of ion movement as ions primarily transport in amorphous phase. The activation energy values obtained from conductivity data for the regions (region-I and region-II) decreases in both un-irradiated and irradiated systems as the ionic conductivity increases which confirm the conduction in these polymer electrolytes is predominantly ionic.
5.2 Scope for future work

This research work presented in this thesis opens up a number of avenues for future research in the field of solid polymer electrolytes. The logical continuation of this experimental research can be extended in several new directions. Due to the concern for the environment impact, the biodegradable polymer which might be a good candidate to replace the conventional liquid electrolyte and polymer electrolyte in order to reduce the impact to environment, in our current study, the polymer electrolytes are generated based on a single type of host polymer. Here HPMC, which is environmental friendly and biodegradable, is used as single host polymer for all polymer electrolyte systems. Thus, for future work, the blending of polymer hosts such as HPMC / PVA, HPMC / PEO / Plasticizers / grafted natural rubber and others might be considered in the development of a solid type of polymer electrolytes.

Different types of dopant salts, such as lithium triflate (LiCF$_3$SO$_3$), lithium hexafluoroarsenate (LiAsF$_6$), lithium tetrafluoroborate (LiBF$_4$) and lithium trifluoromethanesulfonimide (LiN(DF$_3$SO$_2$)$_2$), and also other types of ceramic fillers, such as titanium dioxide (TiO$_2$) and zirconium dioxide (ZrO$_2$) might be incorporated into the polymer host in order to study the effects of different types of dopant salt and ceramic fillers, with the current samples as the reference materials. More characterization methods can be used to enhance the knowledge in this study. The thermal property of the polymer electrolyte can be observed from the results of the Defferential Scanning Calorimeter (DSC) and Thermogravimetric Analysis (TGA) to determine the glass transition temperature (Tg), thermal stability and thermal degradation of the samples. The effects of heavy ion beam irradiation and the effects of neutron rays, gamma rays and charged particles on the optical, thermal, structural and ionic conductivity properties of the polymer electrolytes may be studied. The ionic conductivity at ambient temperature and at different higher doses may be thoroughly studied. Battery characteristics for all polymer electrolytes may be studied thoroughly.