CHAPTER-6

CONCLUSION

This chapter summarizes conclusions emerged out of the experimental techniques.

In this chapter we summarize all the results of the experiments performed in the present investigation of irradiated polymer blend nano-composite electrolyte containing sodium ion. We also present the future scope of further research and possible electrochemical applications of the prepared blend electrolyte materials. In the present work, a methodical study on PEO-PAM polymer blend nano-composite electrolytes containing sodium salt irradiated with swift heavy ion O^{6+} has been undertaken. In this study, for sample preparation, we first optimized the ratio of the polymers, PEO to PAM to understand the effect of blending and then incorporated the optimized sample with different concentrations of sodium salt. After this, addition of different amounts of plasticizers was carried out. We have used 1:1 w/w ratio of two plasticizers EC and PC for our study. Finally, we incorporated different amounts of inert nano-filler SiO_2 in the system. After sample preparation, we characterized all the samples using XRD, SEM, DSC, FTIR and transport number measurement. To understand the conduction and relaxation mechanisms, the samples were subjected to electrochemical impedance spectroscopy. Later, all the samples were irradiated using 80 MeV swift heavy O^{6+} at four different fluences of 1×10^{11}, 3×10^{12}, 1×10^{12} and 2×10^{12} ions/cm^2. All the irradiated samples were also characterized using above mentioned techniques and subjected to electrochemical impedance spectroscopy to investigate the modifications imposed on the electrolyte materials due to irradiation. Results of every study are compared before and after irradiation in the present work.

Vibrational Spectroscopy technique was used to investigate the extent of polymer blending and amalgamation of salt, plasticizers and nano-filler in the polymer matrix. All the samples of PPS system show only two peaks (1633 cm^{-1} and 2059 cm^{-1}) and a broad halo at 3440 cm^{-1}. Peak at 1633 cm^{-1} corresponds to the –C=O stretching vibration mode of PAM which shifted from 1666 cm^{-1}. All other peaks observed for PEO are suppressed and also no peaks corresponding to the triflate salt are observed. Addition of salt gradually leads to decrease in the intensity of the observed peaks. In case of PPSP system, peaks observed at 712 cm^{-1} and 713 cm^{-1} respectively show symmetric ring deformation and ring bending modes of PC and EC respectively. The peaks at 775 cm^{-1}and 777 cm^{-1} are attributed to ring bending and CH_2 rocking and ring breathing modes of EC and PC respectively. The peaks at 890 cm^{-1} and 1076 cm^{-1} show ring breathing mode of EC. 1168 cm^{-1} and 1392 cm^{-1} peaks show C-O-C symmetric stretching and CH_2 wagging of EC whereas CH_2 bending of EC is shown by peak at

1481 cm^{-1}. Peaks at 1791 cm^{-1} and 1808 cm^{-1} show C=O stretching of PC and EC respectively. Intensity of all these peaks decreases with EC+PC content up to 15 wt% and then increases slightly for 20 and 25 wt%. Also, the peaks shift toward low wave-number side in all the cases meaning that the bond length are increasing. Additionally, the peak corresponding to 637 cm^{-1} is observed in the plasticized electrolyte samples contributed by *δa(SO3)*, free triflate anions in sodium triflate salt which was absent in PPS system. All these observations suggest a good amalgamation of all the contents of the electrolytes. Addition of SiO_2 leads to the observation of peaks at 1067 and 3423 which show Si-O-Si asymmetry and O-H stretching of surface hydroxyl groups SiO_2 of respectively. The intensity of the peaks decreases with increase in amount of SiO_2 up to PPSPN-7.5 sample, slightly increase for PPSPN-10 sample, again decrease for PPSPN-12.5 sample and then finally increase for PPSPN-15 sample. All the peaks observed in PPSP system shift away from the actual wave-number suggesting an excellent mixing and formation of nano-composite electrolyte. In each of the above systems, irradiation by SHI, decreases the peak intensities up to the value of critical fluence (1×10^{12} ions/cm^2) and then the intensities are revived at 2×10^{12} ions/cm^2 fluence.

XRD results indicate that the PEO-PAM make a good blend system. In the blend electrolyte samples, absence of any X-ray peak of the sodium triflate salt suggest a complete dissociation of the salt in polymer blend matrix. The crystallinity decreases with increase in sat concentration is lowest for PPS-17.5 sample. The crystallinity of the electrolyte samples further decrease with incorporation of the plasticizers in the system and the sample PPSP-15 shows lowest crystallinity. Addition of SiO_2 further decreases the crystallinity and the sample. PPSPSN-12.5 shows least crystallinity among the samples of all three series. After irradiation, it is observed that up to the value of critical fluence, the crystallinity of the samples decreases, but increase at higher fluence value. The samples with the lowest peak intensity and crystallinity in their respective X-ray spectra depict the highest conductivity.

DSC thermograms of all prepared polymer films show a sharp endothermic peak of melting temperature (T_m) which is the consequence of transition from semi-crystalline to amorphous phase. In all the systems namely PPS, PPSP and PPSPN, the samples with highest amorphousity show the lowest T_m values in their respective systems. The decrease in melting temperature ascribes decrease in crystallinity.

SEM micrographs demonstrate the presence of sharp pores in PPS-17.5 sample which enhances after irradiation, addition of plasticizer beyond 15 wt% leads to an increase in surface roughness and the pores structures decrease. Incorporation of nano-fillers increases the elongation of pores and irradiation further leads to disorderliness in the system by rupturing the polymer chains and formation of new pathways for conduction process.

Ionic transference number (t_i) of polymer films was measured to understand the ionic contribution in the system. The measurements show that the conduction in the electrolytes is primarily due to ions with negligible contribution from the electrons. The ion transference number of highest conducting samples is the highest in each series.

The blend of polymers PEO-PAM is a fairly miscible semi-crystalline host matrix. The results of impedance spectroscopy reveal that that the electrolyte samples showing highest ionic transference number are highest conducting before and after irradiation. Analysis of the dielectric permittivity and electrical modulus are in good agreement with the conductivity measurements.

The frequency dependent conductivity shows characteristic power law behaviour, with variation at higher frequencies. Dispersion of AC conductivity spectra is fitted using Jonscher's universal power law and the exponent ***n*** is found to be less than 1 in each case.

The real part of dielectric permittivity, ϵ'decreases montonically with the increase in frequency and shows saturation at higher frequencies. The dielectric loss, ϵ''varies inversely with frequency. Dielectric studies performed over the entire temperature and frequency regime confirm ionic mobility and polarization phenomenon. The dielectric loss tangent tan δ increases at low frequencies and disperses towards higher frequency side with increase in temperature.

The conductivity relaxation of the system is investigated using electrical modulus formalism. The modulus plots do not show any peaks in the experimental frequency range; hence the onset frequency has been calculated to comment on the modulus behaviour. Increase in value of onset frequency with increase in temperature depicts thermally activated behaviour of the system.

In all the observed experimental results, irradiation by ion beam, enhances the ionic conductivity and the dielectric properties of the system and also modifies the existing features of the electrolyte samples, it does not bring about a complete washout of the observed trend in any of the characterizations. At higher fluences, the electrolyte films show a reverse effect due to crosslinking of chains.

To summarize our entire work, we suggest that the blend of PEO-PAM polymers proves as an excellent host matrix for electrochemical investigations. The prepared blend electrolytes show good miscibility with all the additives in the system. The ionic conductivity increases by addition of plasticizer and nano-fillers in the system and irradiation further increase electrolytic properties of the films. Ionic contribution to the conductivity is maximum in each of the prepared blend electrolyte samples. However, we have not been able to reach a practically applicable conductivity value, further experiments are on to achieve a higher room temperature conductivity with better mechanical strength of the electrolytes for storage application.

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