CHAPTER 7

CONCLUSION

This chapter summarizes all the experimental results observed in the present investigation of polymer nano-composite electrolytes.
In the present investigation, a systematic study on PEO-based polymer electrolytes has been done. For this, in order to find the optimized PEO-silver salt concentration, the AgCF$_3$SO$_3$ amount has been varied in PEO polymer. Thereafter, the amount of nanofiller SiO$_2$ is varied to examine the transport mechanism of this nano-composite polymer electrolyte. Finally, it was plasticized with PEG to further enhance the transport mechanism to PEO-AgCF$_3$SO$_3$-SiO$_2$ polymer electrolyte system. To augment further the silver electrolyte, silver salt as well as nano-filler SiO$_2$ have been replaced by lithium salt LiCF$_3$SO$_3$ and Al$_2$O$_3$ respectively. Characterization of all the samples is performed using FTIR, XRD, DSC, SEM and transport measurements. Effect of nanofiller without/with plasticization on conduction and relaxation mechanism in PEO based polymer electrolytes has been studied.

The change in molecular vibrational spectra due to the interaction of host polymer with salt, nanofiller and plasticizer in the system has been analyzed by FTIR. The characteristic vibrational peaks of PEO at 841, 940, 1057 and 1093 cm$^{-1}$ and a broad band in the wave number range 2700-3000 cm$^{-1}$ are present in all the prepared samples. In addition to this, the presences of the new peaks at 636 and 1028 cm$^{-1}$ confirms the complexation of AgCF$_3$SO$_3$ and host polymer PEO. Addition of nano-filler SiO$_2$ reduces the overall intensity of the system, along with the broadening of C-H stretching band and appearance of new peak around 1736cm$^{-1}$ at higher SiO$_2$ content. Plasticization reduces the amorphousity as compared to nano-system. In the Li$^+$-ion conducting system (PLA-system), LiCF$_3$SO$_3$ and plasticizer PEG make a good complexation with PEO which is is confirmed by the appearance of IR peaks of $\delta_{sh}$ (CF$_3$), $\delta_{s}$ (SO$_3$) and SO$_3$ at 526, 636 and 1033 cm$^{-1}$ respectively. Plasticization of polymer nano-composites also indicates an overall increase in intensity of IR spectra as compared to without plasticizer.

DSC studies provide valuable information about the variation in glass transition temperature $T_g$ and melting temperature $T_m$ of the prepared polymer electrolytes. In the silver salt systems highest conducting samples show lowest $T_g$ value and lowest $T_m$ value in their respective series. While plasticization of polymer electrolytes made the system stiffer. Similarly, in Lithium salt systems i.e., PLA and PLP series, the $T_g$ values are observed to be lower than the systems with plasticizer PEG indicating reduction in flexibili-
ty due to addition of plasticizer in.

XRD results show a significant reduction in the intensity of sharp peak of PEO even at higher concentration of salt which indicates the dominance of amorphous phase. But by the addition of nanofiller SiO₂, the diffraction pattern are observed to shift towards lower angle side with small broadening with decreased intensity, expect x= 25 wt% of SiO₂. An increase in peak intensity is observed on plasticization with PEG compared to that of the PAS series. The addition of nanofiller disturbs the crystalline regions and lead to an increase in the amorphous phase of the system. Whereas, upon plasticization, a significant structural reorganization takes place, leading to an increase in peak intensity as compared to that of the system with nanofiller.

SEM micrographs show the formation of spherulites and reduction in the size of spherulites on addition of salt AgCF₃SO₃ upto 7wt% (PA-7) is observed. Addition of nanofiller in both the system i.e. PAS and PLA improves the uniformity, smoothness and homogeneity of the surface. But on plasticization (PASP and PLP series), surface roughness is the main feature.

The ionic transference number (t_i) of polymer films confirms the conduction mechanism principally due to the transport of ions and the highest conducting sample in their respective represent the highest transference number (in the range of 0.8-0.9 in different systems).

In PEO polymer electrolytes, the addition of PEG plasticizer does not significantly improve the electrical properties in silver ion as well as in lithium conducting systems.

Temperature dependence of dc conductivity follows Arrhenius theory. All the samples with the highest transport number show the highest ionic conductivity. These samples show a power law variation at high frequencies. Dispersion in ac conductivity spectra obeys Jonscher’s power law and the frequency exponent n are found to be smaller than 1.

The real part of dielectric permittivity, ε' decreases with the increase in frequency and saturates at higher frequencies whereas the dielectric loss, ε'' also varies inversely with frequency. The frequency and temperature dependent dielectric studies confirm the ion migration and polarization effects.
The modulus plots confirm the non-Debye behavior and suggest the distribution of relaxation time in the conduction process. Non exponential decay function from modulus spectra provides $\beta$ values are close to 0.5-0.9 and independent of temperature and composition.

The variation of relaxation time $\tau$ with composition is in consonance with the variation in conductivity for PA, PASP and PLP systems, whereas for PAS and PLA systems it is not. Conduction mechanism of the system is mainly affected by the addition of nanofiller not plasticizer PEG.

Coalescing of the data points in the scaling of modulus spectra of PA, PASP, PLA and PLP systems at different temperatures substantiate the fact that relaxation process is temperature independent, while the modulus spectra at different compositions do not merge on master curve which indicates that the relaxation mechanism is composition dependent.

In summary, PEO-based systems make a good polymer composite. All prepared polymer composites show a rise in conductivity on addition of salt, nanofiller and plasticizer. Addition of nanofiller to PA electrolyte system (polymer-salt system) enhances the electrical properties. But the plasticization of PAS system increases the crystalline phase of the system due to similar structure of PEO and PEG. However, lithium ion conducting systems (PLA and PLP) showed higher rise in conductivity as compared to silver ion conducting systems. Hence, lithium ion conducting systems can be used as a good electrolyte.

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