ABSTRACT

In the context of the search for low cost device quality polymer electrolyte with enhanced ambient temperature conductivity for high energy density Lithium Battery Application, the present study on the development of polymer salt complexes based on low cost, commercially available PVC and PVC blends assures significance (or is of significance). The study envisages developing thin films of highly plasticized PVC and PVC/PEG and PVC/PVdF blend systems with LiX salts (X=ClO_4, CF_3SO_3, BF_4) and characterise them using the DSC, XRD, FTIR and A.C. Impedance technique to assess their suitability for Lithium Battery Applications.

To facilitate the A.C impedance measurements, a conductivity cell and a sensitive Microcontroller Based Temperature controller to monitor and control from 40 to 99°C with an accuracy of ±1°C have been designed and facilitated and are presented; the thermal stability of the films has been assessed in terms of the DSC studies and the analysis in terms of glass transition, melting and co-crystalline events are presented. The studies bring out the existence of two glass transition temperatures for the PVC and the PVC blend based systems indicating the existence of two amorphous phases. The identification of these amorphous phases to atatic and syndiotactic phases in the case of PVC based systems is brought out the confirmation of the existence of syndiotactic phase in PVC blend based
system has been given from the FTIR studies. The study brings out the possibility of using the area under the co-crystalline peaks for assessing the crystallinity of systems. The poor miscibility of PVC and the plasticizer, PVC and PEG, not too poor a miscibility of PVC and PVdF and good miscibility of plasticizer and PEG have been brought out by both the DSC and FTIR studies. The complete complexation of the salts in the polymer/blend of the selected systems has been brought out by the absence of a) characteristic pure salt peaks in the FTIR spectra, b) melting peaks corresponding to the pure salts in the DSC spectra and c) the characteristic crystalline peaks of the salts in the XRD. The influence of PVC content/ blend ratio and the nature of the salt on the salt-plasticizer interaction and the influence of the nature of the salt on the anion-polymer interaction and the strong interaction between LiBF$_4$ and PVdF in the blend are brought out by the FTIR analysis. The possibility of breaking of C-Cl bond in the PVC/EC/PC/LiC10$_4$ system with 17.5g PVC content and the attachment of the liberated Cl$^-$ ions with the neighbouring atoms is discussed using the FTIR studies.

The predominantly amorphous nature with some crystallinity of the highly plasticized PVC based and a highly plasticized PVC blend based systems has been arrived at from the XRD results. The influence of the nature of salt annd the PVC content/blend ratio on the crystallinity has
been discussed. Comparing the total peak intensities, the low crystalline complexes have been identified and are presented. They are: PVC/EC/PC/LiBF$_4$ with 7.5g PVC content; PVC/EC/PC/LiClO$_4$ with 7.5g PVC content; PVC/PVdF/EC/PC/LiClO$_4$ with 3/7 PVC/PVdF blend ratio.

The important results that the PVC based systems with low conductivity are capable of giving only modest conductivity are presented. The notable among these systems are the LiBF$_4$ system with 7.5g PVC content giving 0.86x10$^{-4}$S/cm and LiClO$_4$ system with the highest PVC content of 17.5g giving 2.31x10$^{-4}$S/cm as ambient temperature (30°C) conductivity. The range of conductivities obtained at the measurement temperatures lower than the glass transition has been related to the possibility of the existence of non-coupled viscous modes also in ion transport. The temperature behaviour of these systems have been presented.

The low conductivity and inconsistent/irregular behaviour exhibited by the PVC/PEG blend based systems on the variation of conductivity with respect to the blend ratio and salt content have been discussed and the former has been attributed to the high viscosity of the complexes and the latter to indicate the inhomogeneity of the complexes. The unsuitability of PEG as a blend for PVC to enhance the former's conductivity is discussed.
The role of blending PVdF to PVC in enhancing the conductivity is presented through the conductivity data. The PVC/PVdF blend systems giving high and modest ambient temperature conductivities have been identified: they are PVC/PVdF/EC/PC/LiClO₄ with 3/7 PVC/PVdF blend ratios giving a high conductivity of 1.74x10⁻¹⁷ S/cm and PVC/PVdF/EC/PC/LiClO₄ with 5/5 blend ratio and PVC/PVdF/EC/PC/UCF₃SO₃ give conductivities of 2.34x10⁻¹⁵ S/cm and 8.95x10⁻¹⁷ S/cm respectively. The existence of fairly measurable conductivities at temperatures lower than their glass transition temperatures have been discussed interim of the contribution to ionic conductivity by decoupled viscous modes also. The temperature variation interms of Arrhenius VTF behaviour have been presented. The unsratability of PVC/PVdF blend for LiBF₄ presented interms of the conductivity results.

Thus the study shows that from freestanding, thermally stable films with device quality conductivity for Lithium Battery Applications can be developed using highly plasticized PVC and highly plasticized PVC/PVdF blend based systems with LiX (X=C10₄, CF₃SO₃, BF₄) salts.