Chapter 5

Results & Discussion III

5. Thermal Studies

Thermal studies of the polymer electrolyte will provide information regarding their thermal stability and crystallinity. Thermal studies were carried out for the polymer electrolyte samples to find out their thermal parameters, which is important in polymer electrolyte development.

5.1 Differential Scanning Calorimetry (DSC)

The Differential Scanning Calorimetry (DSC) graphs for all the polymer electrolyte samples are shown in Figures 5.1 to 5.3. For comparison, the DSC thermogram of pure polymer (PVDF) and the polymer salt combination, which shows highest conductivity, are shown in Fig. 5.4. The DSC thermogram gives information regarding the melting temperature. This melting point gives information regarding crystalline and amorphous nature of the sample analysed [119]. PVDF is known to be a highly crystalline polymer, which is difficult to plasticize even with a significant amount of liquid organic plasticizers [119,175]. However, the presence of above said plasticizers reduces the crystallinity significantly. All the thermal events occurred in the polymer electrolyte especially the melting temperatures are given in Table 5.1.

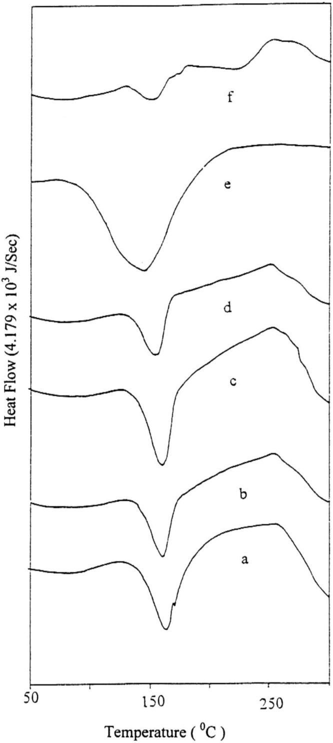

Fig. 5.1. DSC thermograms of DMF plasticizer based polymer electrolytes (a) DMF 1 (b) DMF 2 (c) DMF 3 (d) DMF 4 (e) DMF 5 (f) DMF 6.

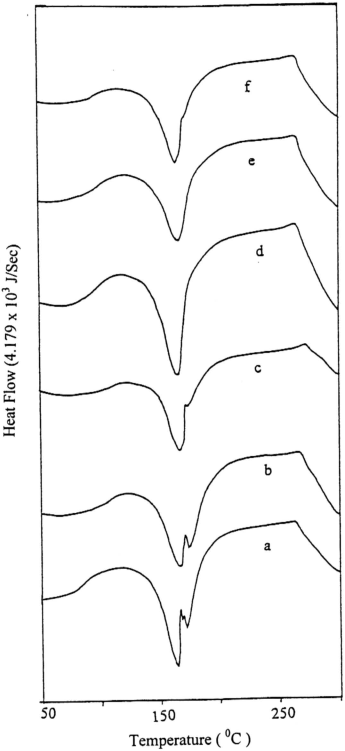

Fig 5.2. DSC thermograms of MF plasticizer based polymer electrolytes (a) MF 1 (b) MF 2 (c) MF 3 , (d) MF 4 (e) MF 5 (f) MF 6

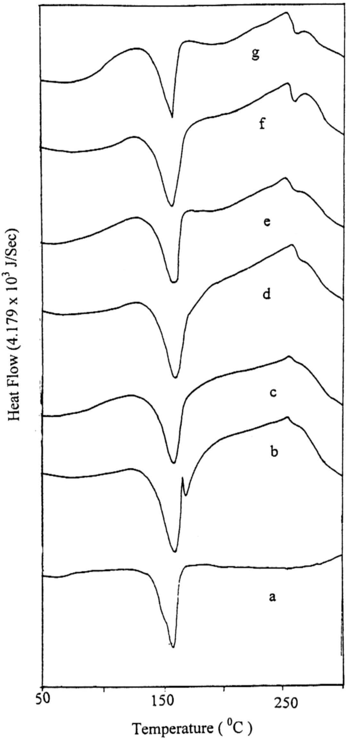

Fig. 5.3. DSC thermograms of EC plasticizer based polymer electrolytes (a) PVDF (b) EC 1 (c) EC 2 (d) EC 3 (e) EC 4 (f) EC 5 (g) EC 6

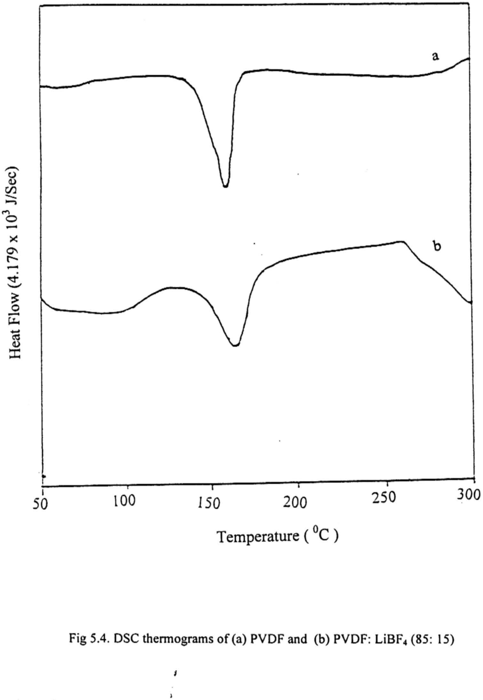

Fig 5.4. DSC thermograms of (a) PVDF and (b) PVDF: $LiBF_4$ (85: 15)

Table 5.1 T_m for different polymer electrolytes

Composition	T_m (in ^0C)	Name
PVDF-$LiBF_4$:DMF (95:5)	162	DMF 1
PVDF-$LiBF_4$:DMF (90:10)	160	DMF 2
PVDF-$LiBF_4$:DMF (85:15)	159	DMF 3
PVDF-$LiBF_4$:DMF (80:20)	153	DMF 4
PVDF-$LiBF_4$:DMF (70:30)	152	DMF 5
PVDF-$LiBF_4$:DMF (60:40)	150	DMF 6
PVDF-$LiBF_4$:MF (95:5)	164	MF 1
PVDF-$LiBF_4$:MF (90:10)	165	MF 2
PVDF-$LiBF_4$:MF (85:15)	165	MF 3
PVDF-$LiBF_4$:MF (80:20)	164	MF 4
PVDF-$LiBF_4$:MF (70:30)	165	MF 5
PVDF-$LiBF_4$:MF (60:40)	164	MF 6
PVDF-$LiBF_4$:EC (95:5)	161	EC 1
PVDF-$LiBF_4$:EC (90:10)	160	EC 2
PVDF-$LiBF_4$:EC (85:15)	161	EC 3
PVDF-$LiBF_4$:EC (80:20)	160	EC 4
PVDF-$LiBF_4$:EC (70:30)	160	EC 5
PVDF-$LiBF_4$:EC (60:40)	160	EC 6
PVDF	160	PVDF
PVDF + LiBF4	164	PVS

The large endothermic peak in the DSC thermograms of the entire polymer electrolyte sample which is ranging from 150^0 C to 165^0C is assigned to the melting of polymer electrolyte samples. This value is in good agreement with the results reported in the literature [119]. Since the melting point of the pure polymer itself is around 160^0C. Thus, in the entire polymer electrolyte samples a large endothermic peak is observed at around that temperature. The DSC thermogram also gives one exothermic peak at around 258^0C for all the polymer electrolyte samples. The exothermic peak, which is at 258^0 C may be attributed to the decomposition of the polymer electrolyte.

5.1.1 Unplasticized Systems

The thermogram of pure PVDF shows very sharp endothermic peak at around 160^0C. When the salt is added to the polymer, the melting peak of the polymer electrolyte broadens and shifts slightly to a higher temperature. This increase in melting temperature of the complex could probably be attributed to the increase in glass transition temperature of the polymer electrolyte. This increase in glass transition temperature may be due to the formation of intra rather than inter chain cross links and that such intra chain cross-linking is largely responsible for the stiffening of the chains and hence the low degree of chain movement. This will lead to an increase in glass transition temperature of the system [51].

5.1.2 Plasticized Systems

5.1.2.1 DMF Based Polymer Electrolyte System

The plot of melting temperature and the DMF content shows very clearly the trend of the plasticized polymer electrolyte system. The plot is shown in Fig. 5.5. The continuous decrease in melting temperature implies that the crystallinity of the polymer electrolyte is reduced considerably.

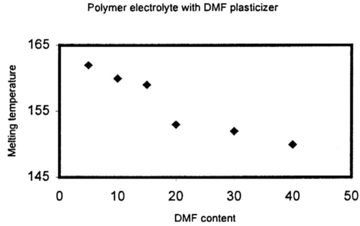

Fig. 5.5. Melting temperature versus DMF content

5.1.2.2 MF Based Polymer Electrolyte System

The plot of melting temperature versus MF content is shown in Fig. 5.6. From Fig.5.6, it can be observed that the melting temperature decrease is not so prominent. This less decrease in melting temperature of the polymer electrolyte samples may be attributed to the fact that the plasticizer is more volatile than the DMF plasticizer and it evaporates slowly while drying.

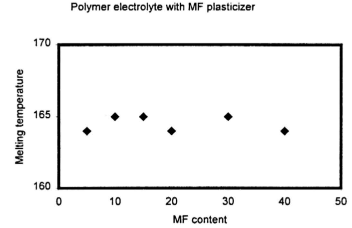

Fig. 5.6 Melting temperature versus MF content

5.1.2.3. EC Based Polymer Electrolyte System

Fig. 5.7 shows the relationship between the melting temperature and the plasticizer composition for EC based polymer electrolyte system. Fig. 5.7 clearly shows the fact that the melting temperature decrease is not uniform and it is not so prominent in this case.

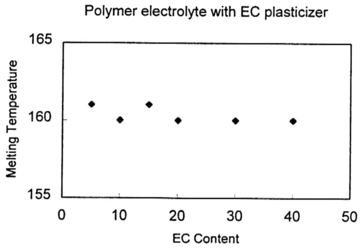

Fig. 5.7 Melting temperature versus plasticizer content

The DSC thermogram of plasticizer based polymer electrolyte DMF1, MF1, MF2 and MF3 shows a small shoulder other than that of the broad endothermic peak at around 160^{0}C. An explanation for this shoulder may be due to the melting of 'free' PVDF, which is not complexed with the lithium salt [176].

From the differential scanning calorimetry studies, it can be observed that the plasticizer DMF shows more depressed crystallinity than the other plasticizers used in the present study. The plasticizer EC also showing the same behaviour as like that of DMF but with less decrease in crystallinity. The polymer electrolyte based on MF plasticizer shows similar melting temperature as like that of the unplasticized system.

5.2 Thermogravimetric Analysis

Thermogravimetric analysis will provide the information regarding the thermal stability of the polymer electrolyte with increasing temperature. The thermal stability of the polymer electrolyte is identified with respect to the mass loss from the TGA graph.

5.2.1 Unplasticized Systems

The TGA plot for the highest conducting polymer salt complex is shown in Fig 5.8. The unplasticized complex shows two mass losses. The first mass loss which is close to 100^0 C may be attributed to the removal of water from the polymer electrolyte. The second mass loss which is at 162^0 C may be due to the melting of the polymer electrolyte sample. Since the polymer electrolyte melts close to that temperature.

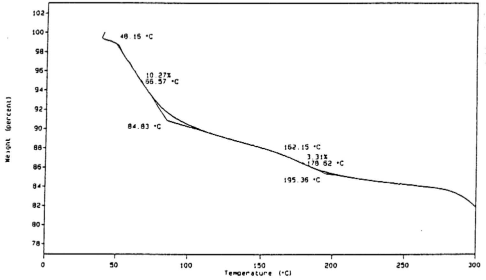

Fig. 5.8 TGA plot for PVDF:LiBF4 (85:15)

5.2.2 Plasticized Systems

Fig. 5.9 to 5.11 shows the TGA traces for polymer electrolytes, which has been prepared using three different kinds of plasticizers. The TGA graph for the entire polymer electrolyte shows mass loss at around 100^0C. This mass loss at 100^0C may be attributed to the water loss in the polymer electrolyte sample. Although the sample is dried for longer time, trace amount of water is present in the sample. The second mass loss in all the samples approximately at around 170^0C to 190^0C may be due to the melting of polymer electrolyte. TGA plots of all the plasticized polymer electrolyte system reveals the fact that polymer electrolyte containing DMF has more mass loss, followed by EC and MF. It indicates that the polymer electrolyte containing MF has more thermal stability than the other plasticizer used in the present study. This high thermal stability of the MF plasticizer based polymer electrolyte may be attributed to the slow removal of plasticizer while drying.

In all the polymer electrolytes, it is observed that increased plasticizer content will decrease the thermal stability. In the case of unplasticized polymer electrolyte sample, the addition of salt did not give much effect on thermal stability. The Table 5.2 gives the information regarding the mass loss with respect to their plasticizer content.

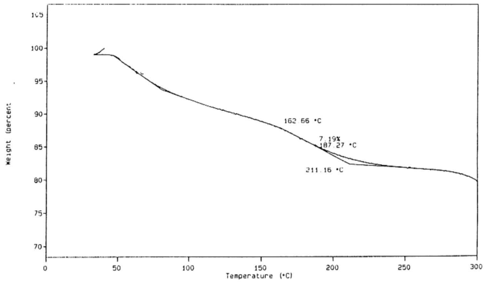

Fig. 5.9 (a). TGA plot for DMF 1

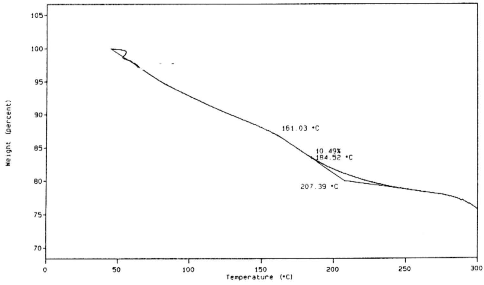

Fig. 5.9 (b). TGA plot for DMF 2

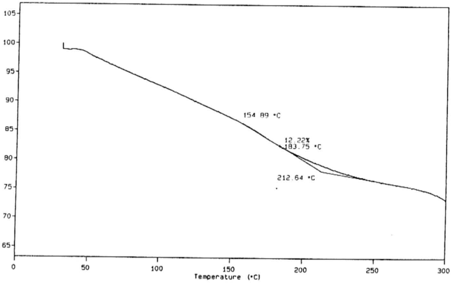

Fig. 5.9 (c). TGA plot for DMF 3

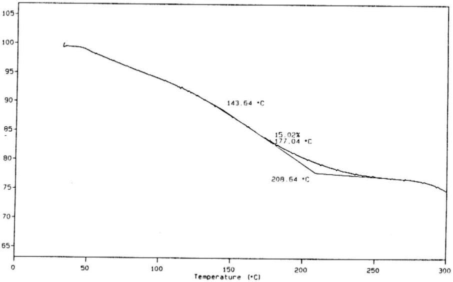

Fig. 5.9 (d). TGA plot for DMF 4

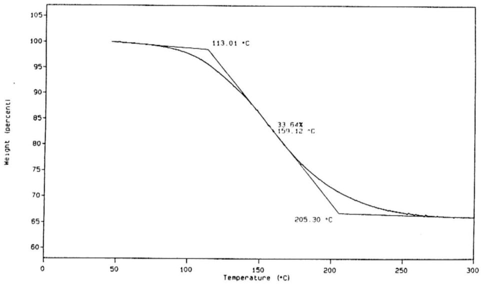

Fig. 5.9 (e). TGA plot for DMF 5

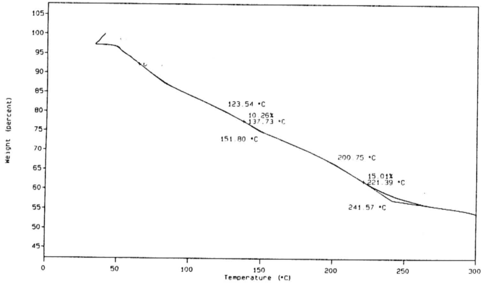

Fig. 5.9 (f). TGA plot for DMF 6

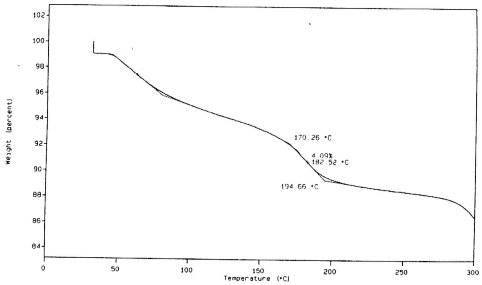

Fig. 5.10 (a). TGA plot for MF 1

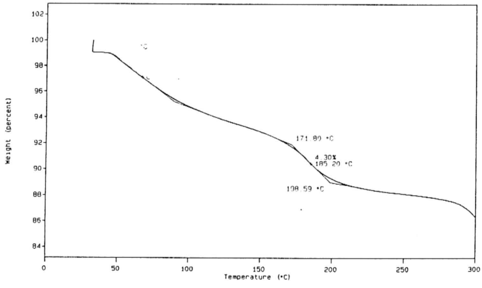

Fig. 5.10 (b). TGA plot for MF 2

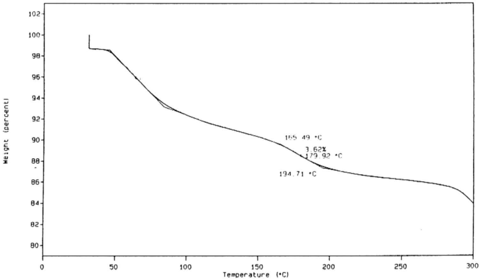

Fig. 5.10 (c). TGA plot for MF 3

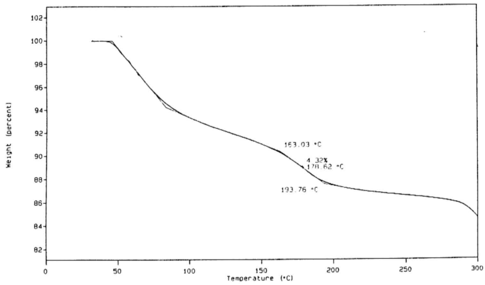

Fig. 5.10 (d). TGA plot for MF 4

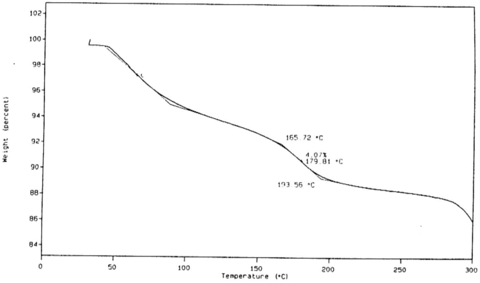

Fig. 5.10 (e). TGA plot for MF 5

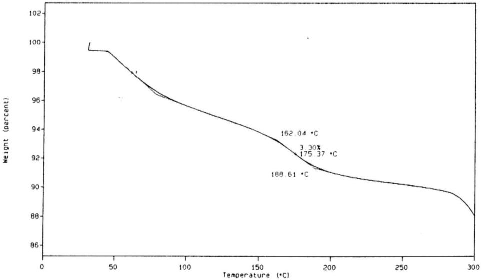

Fig. 5.10 (f). TGA plot for MF 6

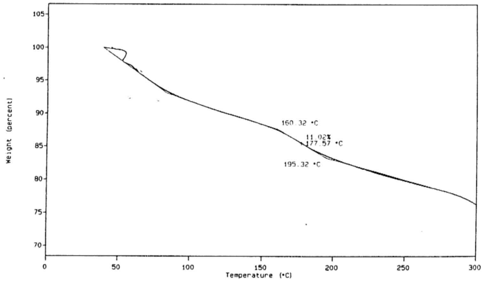

Fig. 5.11 (a). TGA plot for EC 1

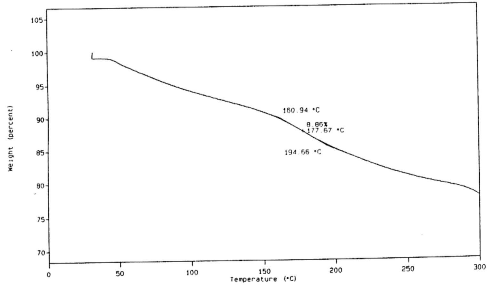

Fig. 5.11 (b). TGA plot for EC 2

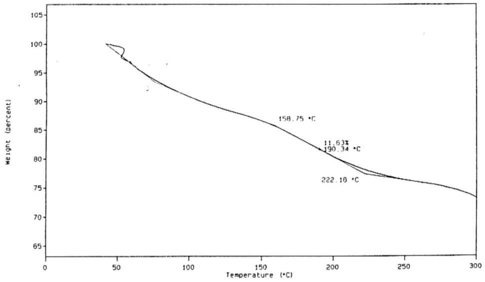

Fig. 5.11 (c). TGA plot for EC 3

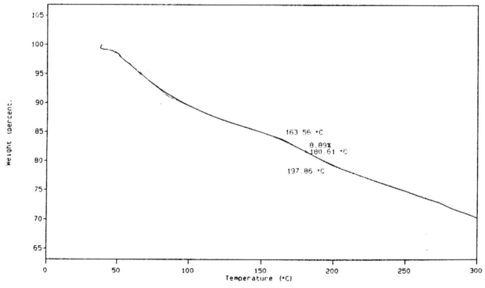

Fig. 5.11 (d). TGA plot for EC 4

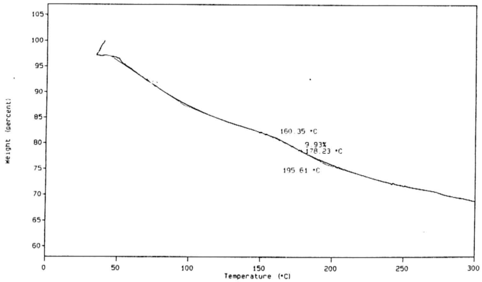

Fig. 5.11 (e). TGA plot for EC 5

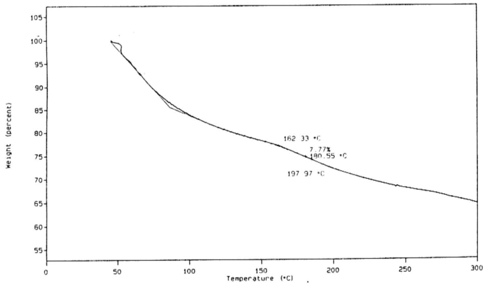

Fig. 5.11 (f). TGA plot for EC 6

Table 5.2 Mass loss observed in different polymer electrolytes at melting

Composition	Mass loss at melting (g)	Name
PVDF-$LiBF_4$:DMF (95:5)	7.19	DMF 1
PVDF-$LiBF_4$:DMF (90:10)	10.49	DMF 2
PVDF-$LiBF_4$:DMF (85:15)	12.22	DMF 3
PVDF-$LiBF_4$:DMF (80:20)	15.02	DMF 4
PVDF-$LiBF_4$:DMF (70:30)	33.64	DMF 5
PVDF-$LiBF_4$:DMF (60:40)	25.27	DMF 6
PVDF-$LiBF_4$:MF (95:5)	4.09	MF 1
PVDF-$LiBF_4$:MF (90:10)	4.30	MF 2
PVDF-$LiBF_4$:MF (85:15)	3.62	MF 3
PVDF-$LiBF_4$:MF (80:20)	4.32	MF 4
PVDF-$LiBF_4$:MF (70:30)	4.07	MF 5
PVDF-$LiBF_4$:MF (60:40)	3.30	MF 6
PVDF-$LiBF_4$:EC (95:5)	11.02	EC 1
PVDF-$LiBF_4$:EC (90:10)	8.86	EC 2
PVDF-$LiBF_4$:EC (85:15)	11.63	EC 3
PVDF-$LiBF_4$:EC (80:20)	8.89	EC 4
PVDF-$LiBF_4$:EC (70:30)	9.93	EC 5
PVDF-$LiBF_4$:EC (60:40)	7.77	EC 6
PVDF	---	PVDF
PVDF + LiBF4	3.31	PVS

5.3 Summary

The thermal studies of plasticized and unplasticized polymer electrolyte system shows very clearly the thermal stability of the polymer electrolyte system. The polymer electrolyte has a melting point ranging from 140^0 C to 165^0 C. DMF plasticizer based polymer electrolyte shows prominent change in their melting point but in the case of MF and EC based system, the change is not so prominent. The thermogravimetric analysis shows very clearly the thermal stability of the polymer electrolyte up to 150^0 C. The polymer electrolyte consists of MF has more thermal stability than the other plasticizer based polymer electrolyte system.