

CHAPTER 7

THERMAL PROPERTIES

CHAPTER 7: Thermal properties for complex formation

7.1 Introduction

The thermal behavior of chitosan-lithium acetate electrolytes was characterized by thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC).

7.2 Thermogravimetric Analysis (TGA)

All the samples were subjected to thermal analysis. A typical TGA run for electrolyte containing Al_2O_3 or CeO_2 as the dispersoid is shown in figure 7.1.

TGA run was performed from room temperature up to 600°C .

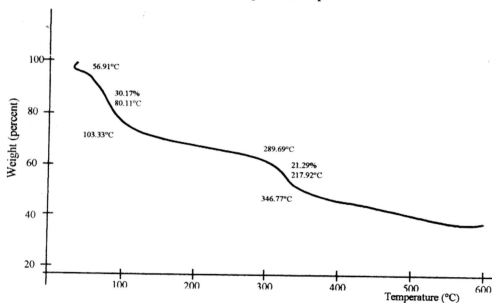
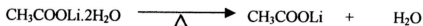


Figure 7.1. A typical TGA thermogram for chitosan-lithium acetate containing Al_2O_3 or CeO_2 as the dispersoid.

TGA plots show that the electrolyte is not stable at high temperature, whereby, around 60% weight loss is observed in the temperature range between 500°C and 600°C.

Figure 7.2 shows the TGA measurements for different concentrations of Al_2O_3 . Figure 7.3 shows the TGA measurement for different concentrations of CeO_2 . As can be seen, there are 3 steps of weight loss process. The maximum weight loss for the three processes started at about 58°C, 285°C and 460°C respectively. These temperatures correspond to the melting temperature of lithium acetate dihydrate ($\text{CH}_3\text{COOLi}\cdot 2\text{H}_2\text{O}$), pure lithium acetate (CH_3COOLi) and lithium hydroxide respectively (refer to the reaction equation below) according to the melting temperature for these chemicals provided by Sigma-Aldrich Chemical Company. When the samples are heated from room temperature, lithium acetate dihydrate begins to melt at 58°C. Further heating the dehydrated $\text{LiOAc}\cdot 2\text{H}_2\text{O}$ yields pure LiOAc which melts at 285°C. Subsequent heating decarbonized lithium acetate and turn it to LiOH , which melts at 460°C. This shows that upon heat treatment, lithium acetate dihydrate will be purified and further heating will change pure lithium acetate into lithium hydroxide. The film is stable until 600°C as no decomposition trend is observed from the TGA scan.



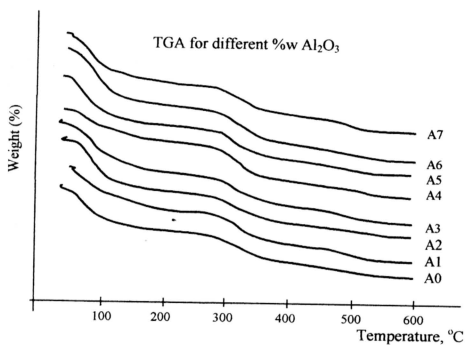


Figure 7.2. TGA measurement for different concentration of Al₂O₃.

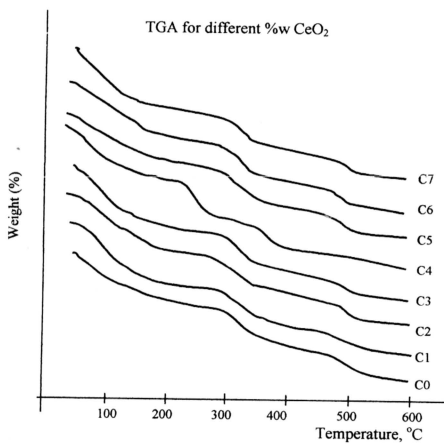


Figure 7.3. TGA measurement for different concentration of CeO₂.

7.3 Differential Scanning Calorimetry (DSC)

DSC for various samples were taken. Figure 7.4 shows the DSC scan for pure chitosan. Pure chitosan shows a glass transition temperature, T_g at 220.35°C. A broad and diffused endotherm around 99.28°C is observed. This is due to water. Clearly, chitosan is an amorphous material and the DSC result supports the XRD result.

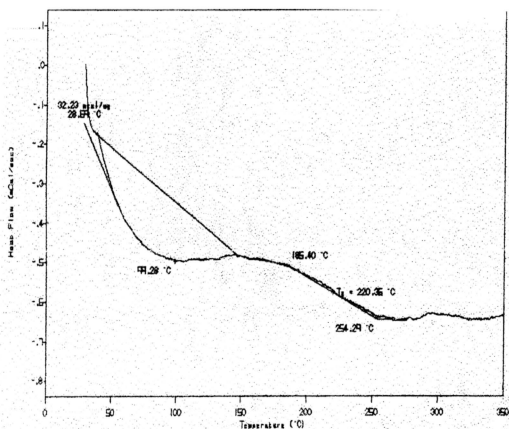


Figure 7.4. DSC scan for pure chitosan.

Figure 7.5 shows a typical DSC scan of chitosan-lithium acetate electrolytes. Figure 7.6 and figure 7.7 shows the DSC scan of chitosan-lithium acetate electrolytes with different weight percentages of Al_2O_3 and CeO_2 respectively from room temperature to 350°C at a rate of $10^\circ\text{C}/\text{min}$. DSC trace for pure chitosan is included for comparison.

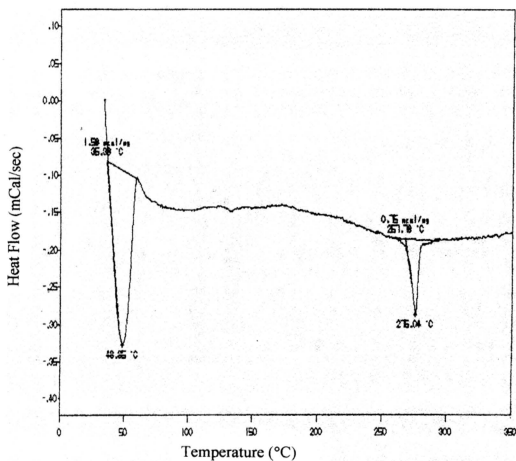


Figure 7.5. A typical DSC scan of chitosan-lithium acetate electrolytes.

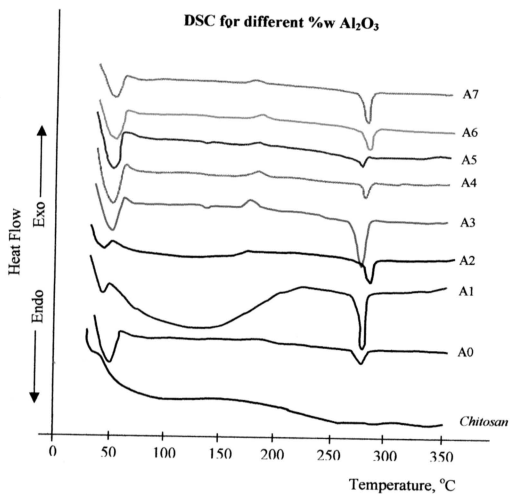


Figure 7.6 DSC scan of chitosan-lithium acetate electrolytes with different weight percentages of Al_2O_3

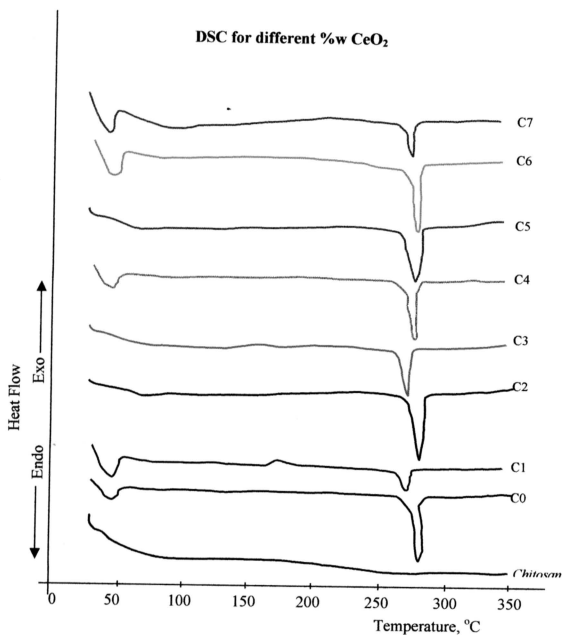


Figure 7.7 DSC scan of chitosan-lithium acetate electrolytes with different weight percentages of CeO₂.

The heat treatment is done from room temperature to 350°C at 10°C/min. The DSC curves with lithium acetate salt have two melting peaks (the endotherm). The first melting peak T_{m1} around 49°C and the other main peak T_{m2} around 277°C. This is around 8°C lower than the temperature obtained in the TGA run. Thus, we can infer that the two melting temperature corresponds to the melting of lithium acetate dihydrate and pure lithium acetate respectively.

No prominent shift of melting peak is observed. No T_g value is observed showing that the samples with added Al_2O_3 and CeO_2 become more crystalline than the host polymer. This has been shown from the XRD results in chapter 6. From figure 7.6, we can see that A2 exhibits the least degree of crystallinity as its melting peaks are shortest. Although XRD may have shown the sample A1 to be more amorphous than sample A2, DSC result have proven otherwise. This helps to justify the conductivity result. There is no relation between the melting heat enthalpy and the crystallinity of the samples as upon heat treatment, it is observed that only the melting peak of lithium acetate is prominent. A very small peak in the electrolyte around 170°C may be associated with a formation of new crystalline complexes. No decomposition trend is observed within the thermal treatment range of the electrolytes samples. The average melting temperature for Al_2O_3 complexes are 49.9°C and 276.3°C, while for CeO_2 complexes are 47.3°C and 278.3°C.

7.4 Summary

Both TGA and DSC run show the changes of lithium acetate upon heat treatment. No transition temperature is observed for all the samples with added dispersoid (Al_2O_3 and CeO_2), showing that the samples become more crystalline upon addition of dispersoid. A2 has the lowest melting energy showing the least crystallinity nature. From DSC result for A1, we are certain that sample A1 has a lower conductivity than sample A2 as have been measured in chapter 5. The addition of Al_2O_3 or CeO_2 does not make the chitosan-lithium acetate samples more stable thermally.
