Thermal and Conductivity Studies of Chitosan Acetate-Based Polymer Electrolytes

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Abstract. Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) have been employed to study the thermal stability of the chitosan acetate-based polymer electrolyte films. The glass transition temperature, T_g measurements confirm the conductivity enhancement effect by adding the plasticizer and salt in the chitosan acetate films

1. Introduction

Chitosan is a polymer of β-1,4-linked 2-amino-2-deoxy-D-glucopyranose and has been used extensively for various industrial and medical applications [1-4]. It can be derived by deacetylation of chitin or obtained from the cell walls of living things such as Phycomyces blakesleeanus. Its ability to form complexes with various metal ions has been explored in several studies as a natural chelating agent [5-7].

It is well known that polymer-lithium electrolytes have a potential application in solid-state batteries [8-14]. In the effort to find alternative polymers to act as electrolyte in solid-state polymer batteries, chitosan was studied [15-17]. To quote some of the work that have been done on the thermal properties of chitosan, consider the work of Sakurai et al. [18-19] that reported the glass transition temperature, T_g of chitosan being ~203 °C. The measurement of T_g is important since it is related in some ways to the conductivity of the polymer. According to Forsyth et al. [20-21] plasticizers are able to reduce the T_g of the polymer. The reduction in T_g increases the chain mobility, which leads to conductivity enhancement. Hence, the increase in conductivity with increasing amount of plasticizer should be accompanied by a reduction in T_g. It has been reported [22] that T_g increases rather slowly in the PPO-$NH_4CF_3SO_3$-PPG4000 complex with salt concentration and increases rapidly at high salt concentrations T_g. The drastic increase in T_g is accompanied by the lowering of conductivity. A similar observations on the ionic conductivity of the polymer electrolytes based on phosphate and polyether copolymers has been reported by Seong et al. [23]. At low salt concentration the increase in conductivity is accompanied by an increase in T_g. When the amount of salt increases, T_g increases quite drastically which is accompanied by the drop in conductivity.

In this work, the effect of adding plasticizer and salt to the chitosan acetate films on the thermal properties will be studied using TGA and DSC techniques. The glass transition temperature, T_g, of the chitosan acetate-based films will be determined and the relationship between the glass transition temperature, T_g, and ionic conductivity will be established. To the knowledge of the authors, there is no report on the T_g variation in chitosan-salt and chitosan-salt-plasticizer complexes so far.

2. Experimental Description

2.1. Sample Preparation. 1 g of chitosan (6×10^5 g/mol, Fluka) was dissolved in 100 ml 1% acetic acid solution. Lithium triflate ($LiCF_3SO_3$) and ethylene carbonate (EC) were added accordingly. After complete dissolution, the solutions were cast in petri dishes and left to form films of pure chitosan acetate (CA), plasticized chitosan acetate (CA-EC), salted chitosan acetate (CA-$LiCF_3SO_3$) and salted-plasticized (CA-EC-$LiCF_3SO_3$) at room temperature. The films were then transferred into a dessicator for continuous drying.

2.2. TGA and DSC Measurements. Thermogravimetric (TGA) measurements were recorded using the Rheometric Scientific TGA 1000 at a heating rate of 10 °C min^{-1}.

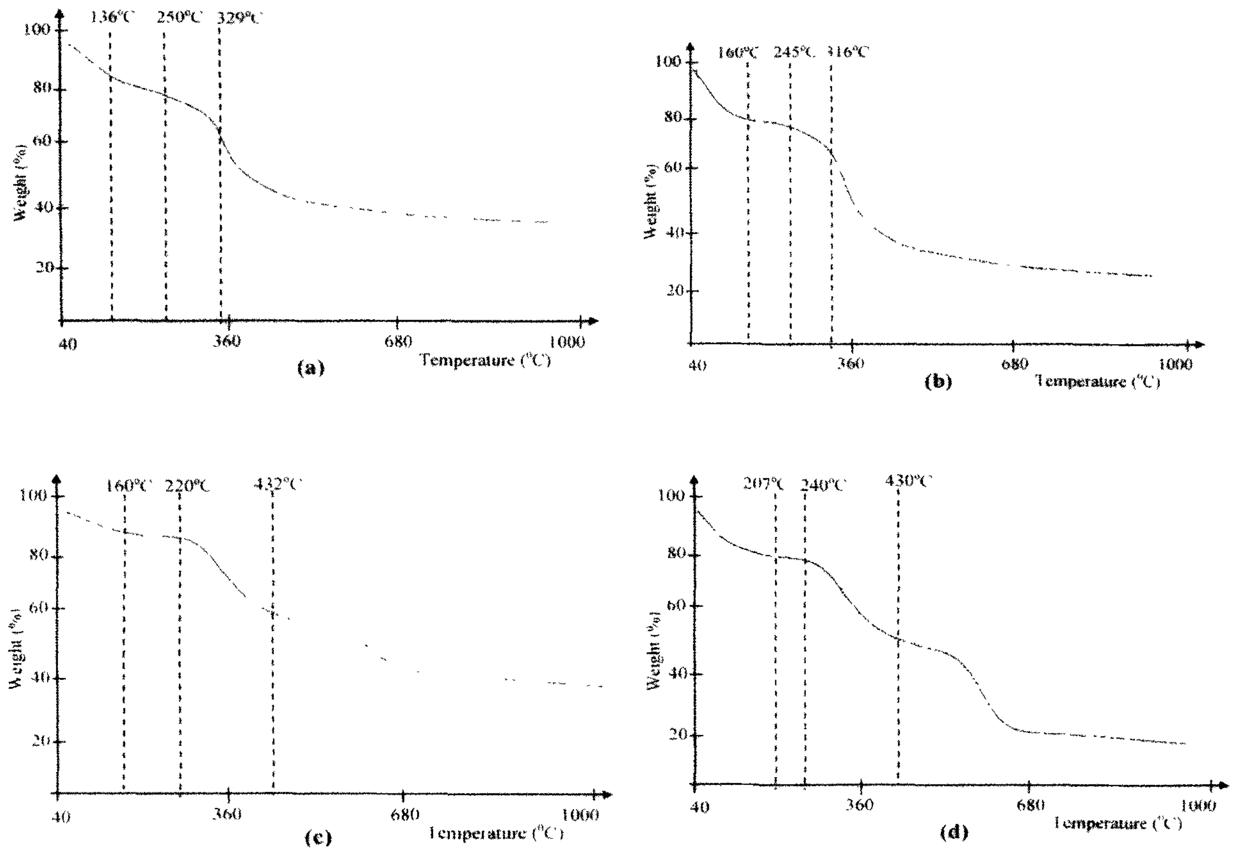

Fig. 1. TGA traces for (a) pure CA (b) plasticized CA (c) salted CA and (d) salted-plasticized CA films.

Differential Scanning Calorimetry (DSC) measurements were performed using the Rheometric Scientific DSC (LN) also at a heating rate of 10 °Cmin^{-1}. T_g was estimated from the DSC curves obtained from the second heating run after the first run of heating up to 350 °C and cooling to 25 °C at a cooling rate of 10 °Cmin^{-1}.

2.3. Ionic Conductivity Measurements. Electrical conductivity measurements were performed with a HIOKI 3531-01 LCR bridge that has been interfaced with a computer in the frequency range 42 Hz to 5 MHz. The electrical conductivity of the sample, σ, can be calculated using the equation $\sigma = t/(R_bA)$ where t is the thickness of the film, A is its cross-sectional area and R_b is the bulk resistance obtained from the Cole-Cole plot for each sample [24].

3. Results and Discussion

3.1. TGA and DSC. The TGA curves representing the different stages of pure CA, plasticized CA, salted CA and salted-plasticized CA films are shown in Figs. 1(a), (b), (c) and (d), respectively. The DSC traces for these films are shown in Figs. 2(a), (b), (c) and (d). From Fig. 1 in the first stage the weight loss is attributed to absorbed water and/or water in the dilute acetic acid solvent used to dissolve the chitosan powder and also due to the plasticizer, ethylene carbonate (Fig. 1(b) and Fig. 1(d)) with ~16% and ~17% of weight loss, respectively. These results correspond to the endothermic peak in the DSC traces as shown in Fig. 2 and are consistent with weight loss values reported by Ritthidej et al. [2] and Ratto et al. [25]. For the pure chitosan acetate sample the endothermic band has a peak at ~50 °C. However in the plasticized CA film the endothermic band consists of two peaks. The first peak at ~51 °C is attributed to EC while the second peak at ~64 °C is attributed to the residual water present in the sample [26]. The addition of EC has shifted the peak of this band from ~50 °C to ~64 °C. The endothermic band peak has increased to ~61 °C for the salted CA film from ~50 °C for the unsalted film. The introduction of the salt on the CA film has increased the temperature at which the endothermic band peaked. The peak has further shifted to ~72 °C for the salted-plasticized

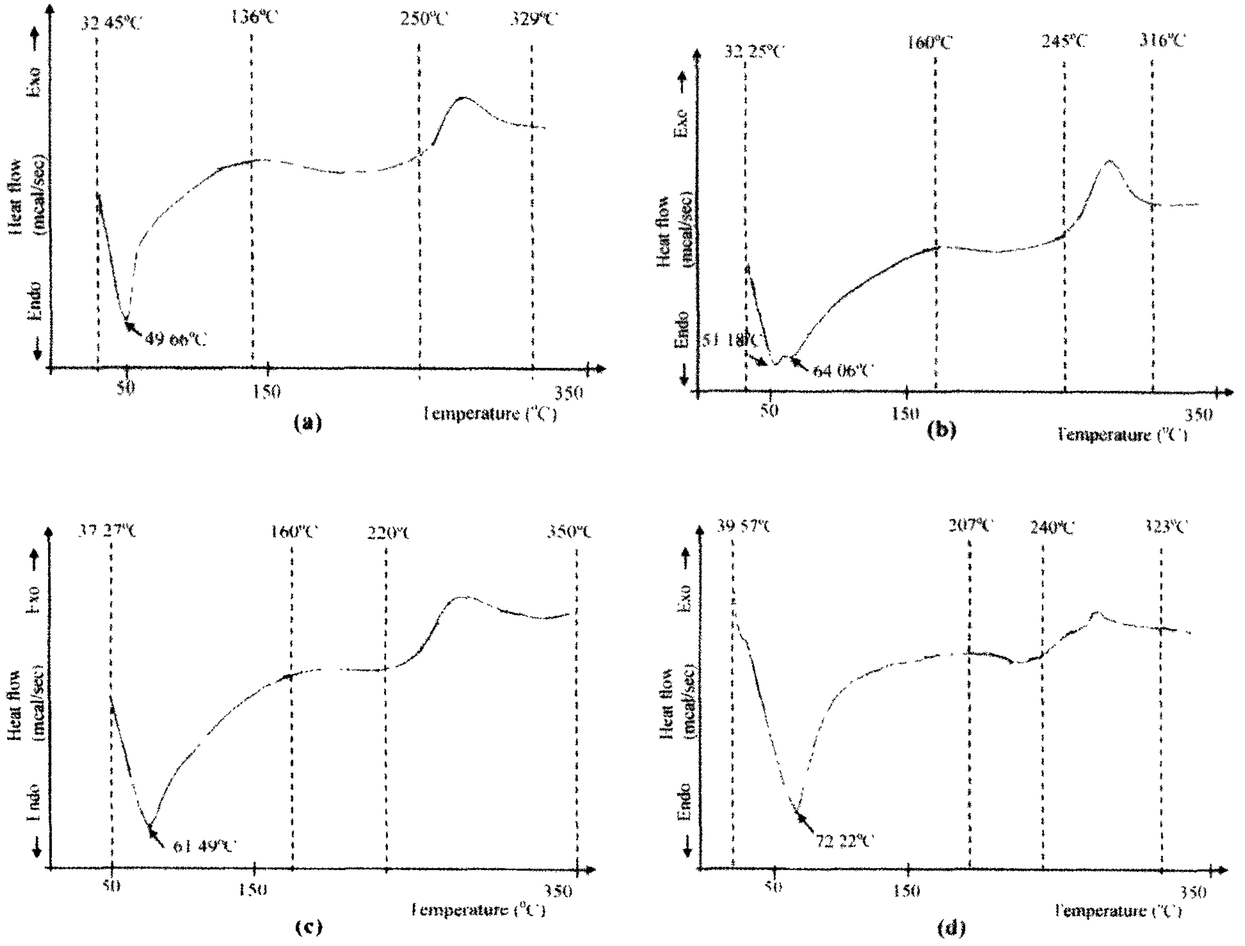

Fig. 2. DSC traces for (a) pure CA (b) plasticized CA (c) salted CA and (d) salted-plasticized CA films.

CA film from ~61 °C for the plasticized CA film. According to McNeill and co-workers [27], the loss in weight inthe temperature range 136 up to 250 °C in the TGA trace (Fig. 1(a)) there is ~5% weight loss which is attributed to the loss of acetic acid in the polymer, and according to them a small fraction of the acetate group can still be present in the polymer up to 400 °C. This is confirmed by the DSC plots in Fig. 2(a). The DSC traces do not show an endothermic band from 160 to 245 °C, 160 to 220 °C and 207 to 240 °C for the plasticized sample, salted sample and salted-plastized sample, respectively as shown in Figs. 2(b) to 2(d). The TGA traces are quite flat in these temperature ranges indicating small weight losses for these samples.

Sakurai et al. [18] have reported that chitosan begins to degrade at 250 °C. This could be the reason for the presence of an exothermic band in the DSC traces in the temperature range between 220 °C up to 350 °C. Plasticization seems to enhance the decomposition of the chitosan complex film where the sample begins to degrade at 245 °C as shown in Fig. 1(b). It can be observed that for the salted CA and salted-plasticized CA samples, TGA traces show further weight losses after 400 °C, which could be due to decomposition of the lithium triflate salt.

3.2. Relationship Between T_g and Ionic Conductivity. In this work, films from a fixed amount of plasticizer (EC) but different amounts of lithium triflate were prepared. Figure 3 represents the relationship between T_g and the conductivity of these films. It can be observed that T_g decreases with increasing conductivity.

These results imply that an increase in concentration of salt in the plasticized film up to an optimized concentration will increase the motion in some parts of the polymer chain, which will reduce T_g and increase the conductivity. However, the increase in T_g when the salt

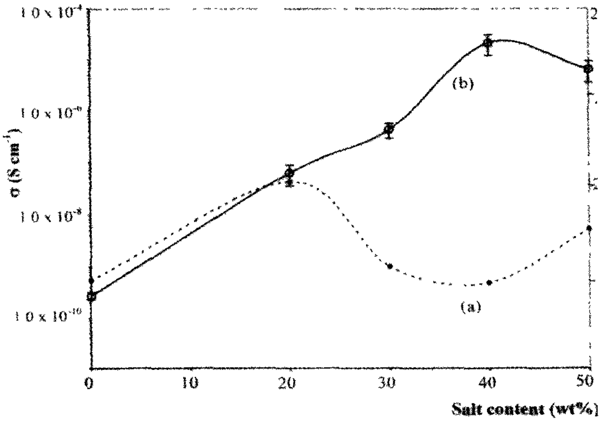

Fig. 3. Glass transition temperature, T_g (a) and conductivity for the salted-plasticized chitosan acetate films versus salt content (b).

concentration is greater than that of the conductivity-optimizing amount is due to the decrease in segmental flexibility and the polymer backbone becoming more rigid. The rigidity of the backbone could be due to the formation of cross-links between the cation of the salt with surrounding chain segments that could also reduce the mobility of the cation [22].

4. Conclusions

The TGA and DSC measurements confirm the effect of adding the plasticizer and the salt on the chitosan acetate films. These effects correspond with the value of ionic conductivity of chitosan acetate-based polymer electrolyte systems. The conductivity increases when more salt is added to a plasticized chitosan sample can be explained in terms of the decrease in T_g until a certain optimized concentration is achieved.

5. Acknowledgements

The author would like to thank the University of Malaya for the vote F014/2004A.

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Paper presented at the International Conference on Functional Materials and Devices 2005, Kuala Lumpur, Malaysia, June 6 - 8, 2005.

Manuscript rec. Aug. 5, 2005; acc. Sept. 29, 2005.