CHAPTER 5

ELECTRICAL PROPERTIES

CHAPTER 5: Electrical properties for complex formation

5.1 Introduction

A study reported that the Al_2O_3 dispersal affects the conductivity and polymer matrix crystallite size (Chandra and Chandra, 1994a). Liang (1973) is the first to study the conductivity of dispersed phase polycrystalline LiI containing aluminium oxide, where he found that the incorporation of Al_2O_3 substantially increased the conductivitry of LiI. Since then many workers have dispersed ionic conductors (Plocharskiet al., 1989; Capuaro et al., 1991) and ceramic fillers (Wieczorek et al., 1990). It was found that the conductivity was enhanced in comparison with pure compounds. Kadrgulov and coworkers (1996) showed that the addition of Al_2O_3 increases the electrical conductivity of the low-temperature phase for Cu_2Se-Al_2O_3 composite solid electrolyte. CeO_2 has been used as a dispersoid and the effect seems very similar to alumina dispersed composites, where the pronounced changes in conductivity values have been observed (Jacob et al., 1996).

In chapter 4, FTIR spectroscopy has shown that a complex is formed between chitosan and the lithium acetate salt with and without dispersoid (Al_2O_3 and CeO_2). In this chapter, the electrical conductivity of the samples will be measured using Impedance Spectroscopy. It has been known for some time that the nominal addition of inert inorganic ceramic oxides as fillers into polymer electrolytes during the casting procedure improves the conductivity as well as mechanical integrity (Michael et al., 1997).

5.2 Conductivity Variation with dispersoid concentration/composition

From the plot of negative imaginary impedence versus real impedance with the horizontal and vertical axes having the same scale, the bulk resistance, R_b can be obtained.

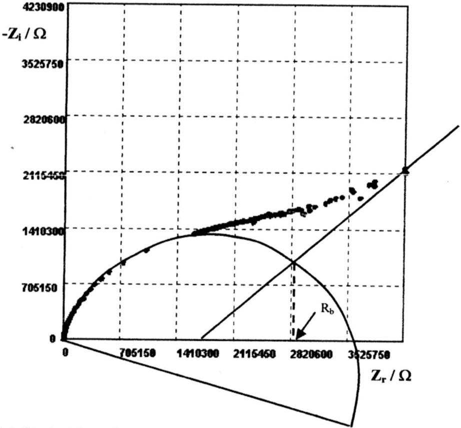

Figure 5.1. Typical impedance plots for the sample prepared.

Figure 5.1 shows typical impedance plots for the sample prepared. Whenever R_b was difficult to obtain from the complex impedance data, the impedance data were converted into admittance data and plotted according to the admittance formalism from which $\frac{1}{R_b}$ may be easier to obtain (Osman et al., 2001). Figure 5.2 shows a typical admittance plot for one of the samples prepared.

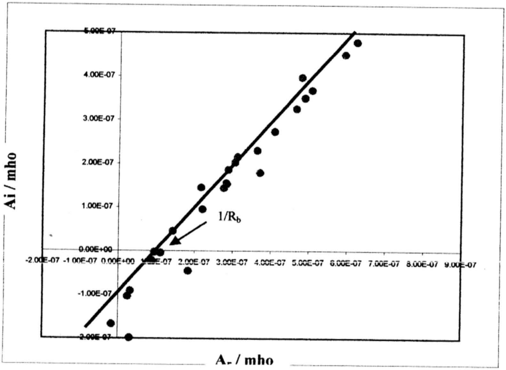

Figure 5.2. Typical admittance plot for one of the samples prepared.

Figure 5.3 shows the plot of conductivity versus wt% of aluminium oxide added. The dispersoid containing film with 2 wt% has the highest conductivity at 8.92 X 10^{-9} Scm^{-1}. For the film without aluminium oxide, the room temperature conductivity value is 3.14 X 10^{-10} Scm^{-1}. On addition of aluminium oxide, the conductivity of film increases. It can be inferred that the dispersoid is responsible for the enhancement of the conductance of the chitosan-lithium acetate films, as with addition of Al_2O_3, the conductivity increases. However, the conductivity becomes less with further addition of Al_2O_3. This is obvious where the conductivity value for sample A4 to A7 is in the same order as the sample with no Al_2O_3 added. As discussed in chapter 4, the complexation occur between chitosan and LiOAc with and without Al_2O_3 added. The complexation is less with 4 wt% of Al_2O_3 and above. This is corresponding to the low conductivity value obtained for sample A4 till A7, where complexation is minimal. The highest conductivity is reached for sample with 2 wt% Al_2O_3 added. The conductivity is approximately 28 times of the film sample without dispersoid added (aluminium oxide in this case). For the sample with 3 wt% Al_2O_3 added, the conductivity is about 50% lower than the conductivity exhibited by the film added with 2 wt% Al_2O_3. This probably due to the inability of the fixed chitosan volume by comparison to assimilate more ions. Ionic conduction in polymers was caused by the diffusion of carrier ions through their free volume (Tsunemi et al., 1982; Tsunemi et al., 1983). However, the conductivity decreases when more Al_2O_3 is added. It reaches the same magnitude at 4wt% Al_2O_3 and above. The drop in conductivity might be attributed to the increasing crystalline nature of the films. To justify this, x-ray diffraction will be carried out and the result will be discussed in the next chapter. The decrease in conductivity also reflects a decrease in the number of mobile ions in the films. Table 5.1 shows the conductivity values for all samples prepared in investigating the effect of Al_2O_3 as dispersoid to the chitosan-lithium acetate electrolytes.

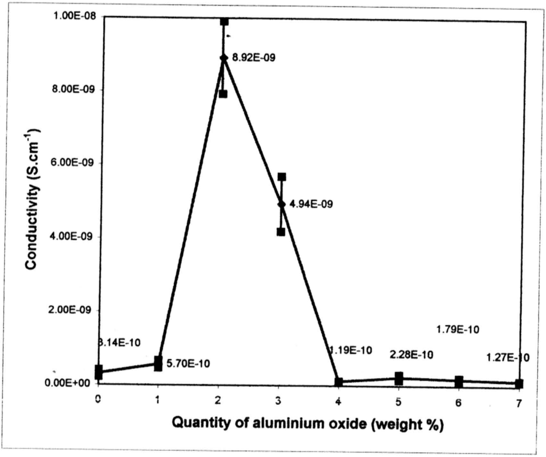

Figure 5.3. Conductivity versus weight percent of aluminium oxide added for chitosan-lithium acetate electrolytes.

Table 5.1. Conductivity for films prepared from different weight % of aluminium oxide in chitosan-lithium acetate electrolytes at room temperature.

Sample	Weight % of aluminium oxide	Average conductivity ($\times 10^{-10}$ S.cm^{-1})
A0	0	3.14 ± 0.94
A1	1	5.70 ± 1.02
A2	2	89.2 ± 9.90
A3	3	49.4 ± 7.5
A4	4	1.19 ± 0.04
A5	5	2.28 ± 0.76
A6	6	1.79 ± 0.41
A7	7	1.27 ± 0.18

In all graphs, the values are averages of 6 sets of data obtained from 6 sets of impedance measurements.

Figure 5.4 shows the plot of conductivity versus the amount of cerium oxide added in wt%. The dispersoid containing films with different wt% CeO_2 exhibit the same magnitude of conductivity. No significant enhancement in conductivity is observed. This result could also be consistent with the FTIR results which have shown that there is very little interactions between CeO_2 and the chitosan-lithium acetate complex. Such little interaction is manifested as insignificant changes in room temperature electrical conductivity of the chitosan-lithium acetate-CeO_2 complexes.

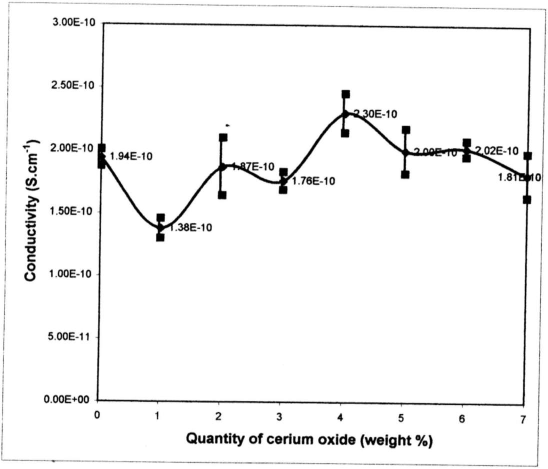

Figure 5.4. Conductivity versus weight percent of cerium oxide added for chitosan-lithium acetate electrolytes. The conductivity value is a mean of six impedence spectroscopy measurements.

Table 5.2 shows the conductivity values for all samples prepared in investigating the effect of CeO_2 as dispersoid to the chitosan-lithium acetate electrolytes.

Table 5.2. Conductivity for films prepared from different weight % of cerium oxide in chitosan-lithium acetate electrolytes at room temperature.

Sample	Weight % of cerium oxide	Average conductivity ($\times 10^{-10}$ S.cm^{-1})
C0	0	1.94 ± 0.06
C1	1	1.38 ± 0.08
C2	2	1.87 ± 0.23
C3	3	1.76 ± 0.07
C4	4	2.30 ± 0.16
C5	5	2.00 ± 0.18
C6	6	2.02 ± 0.06
C7	7	1.81 ± 0.18

In previous work, Yahya (1999), it has been shown that films with 1g chitosan and 0.8g lithium acetate reaches a conductivity value of 7.57×10^{-6} Scm^{-1}. In that work, all films contain a fixed content, 0.4g EC (Ethylene Carbonate) as a plasticizer. This higher conductivity obtained might be due to the addition of plasticizer, which has disrupted the crystallinity nature of the sample ands has helped to increase the degree of dissociation of the salt resulting more mobile ions in the complex. In addition, Yahya has shown that the samples were amorphous from his XRD study.

Figure 5.5(a) and figure 5.6(a) show the impedance plots while figure 5.5(b) and figure 5.6(b) show the admittance plots for all samples prepared in this work involving dispersoid Al_2O_3 and CeO_2 respectively.

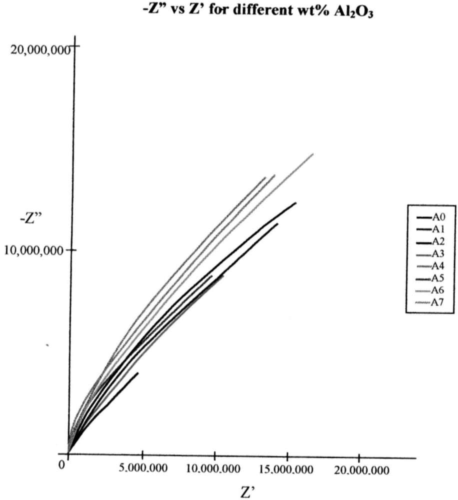

Figure 5.5(a). Impedance plot for different weight percent of Al_2O_3 added chitosan-lithium acetate films

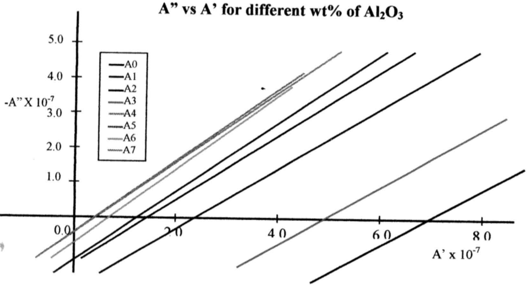

Figure 5.5(b). Admittance plot for different weight percent of Al_2O_3 added chitosan-lithium acetate films

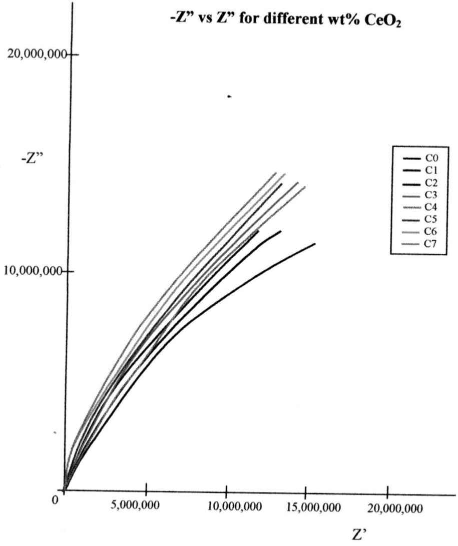

Figure 5.6(a). Impedance plot for different weight percent of CeO_2 added chitosan-lithium acetate films

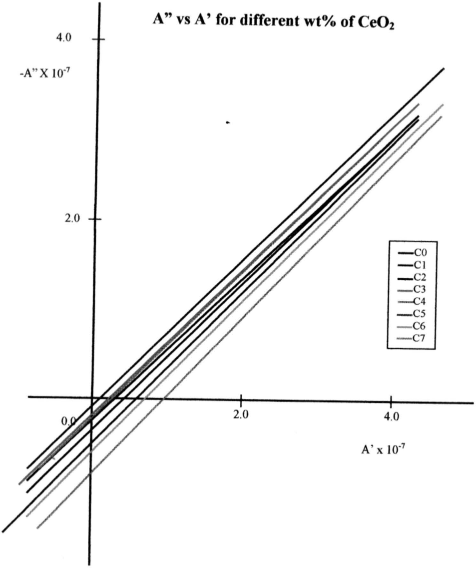

Figure 5.6(b). Admittance plot for different weight percent of CeO_2 added chitosan-lithium acetate films

The mechanism of conductivity enhancement in polymer electrolytes due to ceramic additives remain uncertain (Michael et al., 1997). The proposed mechanism of conductivity enhancement in polymer complexes due to dispersoid is that the dispersoid reduces the host polymer crystallinity which, in turn, enhance the conductivity (Michael et al., 1997). This can be proven by XRD. The results will be exhibited in the next chapter.

5.3 Dielectric Behavior

Impedance Spectroscopy measurements are often performed to determine the bulk conductivity of a sample. Additional information on the material can be obtained from a dielectric analysis, where measurements are performed over a wide frequency range.

Information on relaxing dipoles in the sample may be obtained from an analysis of the complex permittivity since the appearance of a peak in the imaginary part of the permittivity indicates that energy is absorbed by dipoles in the sample. The relaxation frequency and the strength of the relaxation are characteristics of the relaxing dipoles (Mellander and Albinsson, 1996).

Figure 5.7 shows the dielectric constant, ε' versus frequency plots. The dielectric constant plays a fundamental role in the ability of a polymer to dissociate salts (Wintersgill and Fotanella, 1987). With increasing Al_2O_3 content and for a fixed frequency, the value of ε' for the film increases till 2 wt% Al_2O_3. This shows that the dispersoid (Al_2O_3) has increased the dielectric constant of chitosan and increased its ability to dissociate the salt. Therefore the number of mobile ions in the sample increased. Since conductivity is proportional to the number of mobile ion, the conductivity increased. As can be observed from figure 5.7, ε' for A2 is more than 3 times that of A0 and A3 in about 1.5 times that of A0. A1 and A0 has conductivity of the same order of magnitude. The ε' versus log f for these samples are about the same. Hence it can be inferred that the presence of appropriate amounts of Al_2O_3 does increase the room temperature electrical conductivity by helping to dissociate the salt and therefore increasing the number of mobile ions.

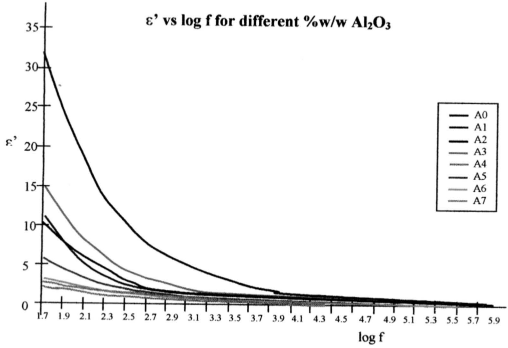

Figure 5.7 Dielectric constant versus frequency for chitosan-lithium acetate complexes with different concentration of Al_2O_3.

Dielectric constant plots for chitosan-lithium acetate complexes with added CeO_2 is shown in figure 5.8. Here we can see minimal difference in its dielectric constant for different concentrations of CeO_2 with its small scale shown. This is observed in the impedance plot. This is why the conductivity of the samples do not vary significantly.

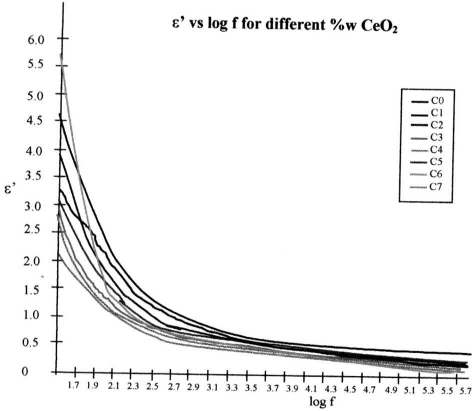

Figure 5.8 Dielectric constant versus frequency for chitosan-lithium acetate complexes with different concentration of CeO_2.

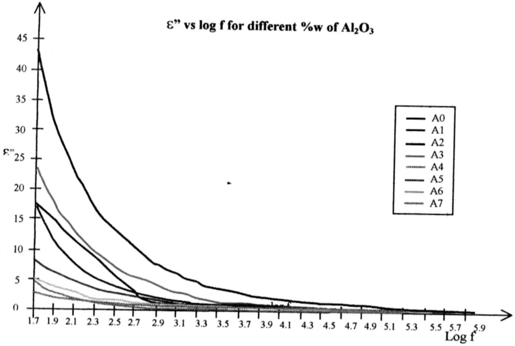

Figure 5.9 Dielectric loss versus frequency for chitosan-lithium acetate complexes with different concentration of Al_2O_3.

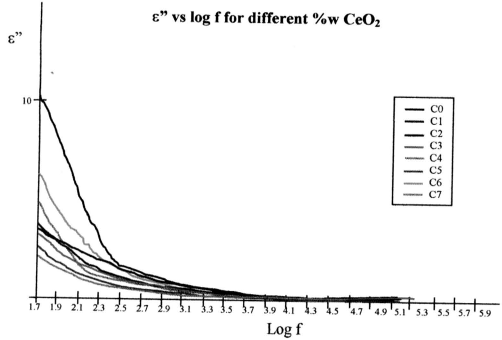

Figure 5.10 Dielectric loss versus frequency for chitosan-lithium acetate complexes with different concentration of CeO_2.

Figure 5.9 and figure 5.10 show the dielectric loss-frequency plots for Al_2O_3 and CeO_2 respectively. In order to verify the presence of residual water, the impedance data was transposed into real and imaginary permittivity data. According to Wintersgill and Fontanella (1987), the dielectric loss, ε" probes a wide variety of phenomena along with any relaxation which may be present in the material. It is therefore expected that if water is present, a relaxation peak can be observed in the dielectric loss (ε")-frequency plots. Since no significant relaxation peak is observed in figure 5.9 and 5.10, it is therefore inferred that residual water does not contribute towards the electrical conductivity of samples added with Al_2O_3 or CeO_2.

Figure 5.11 and figure 5.12 show the real part of electric modulus, M' versus frequency. M' tends to 0 as ω tends to 0. The relaxation peak observed must represent an ionic conductivity relaxation occurring in the systems (Meakin et al., 1997). Since M is reciprocal of ε, the highest conducting sample is the bottom most line. In these plots, there is tailing effect indicating that the material is not very capacitive (Osman et al., 2001) for both Al_2O_3 and CeO_2 samples. The shoulder presents the distribution of relaxation times of the free charges (Mishra et al., 1998).

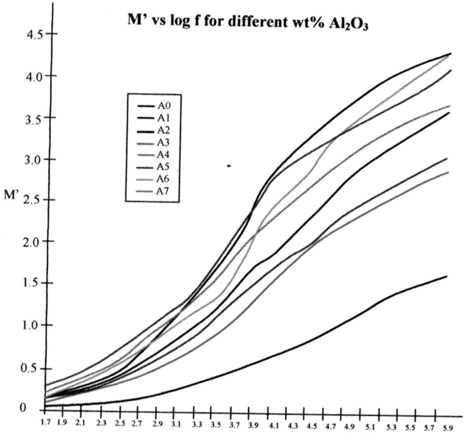

Figure 5.11 Real part of electric modulus versus frequency for chitosan-lithium acetate complexes with different concentration of Al_2O_3.

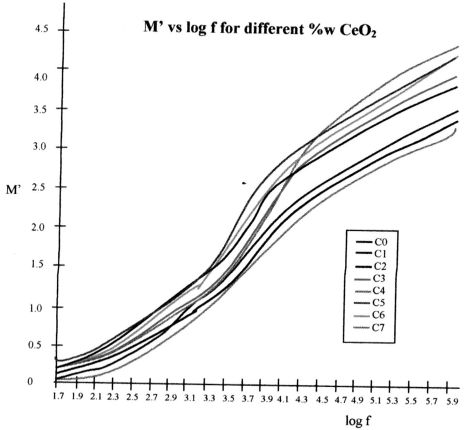

Figure 5.12 Real part of electric modulus versus frequency for chitosan-lithium acetate complexes with different concentration of CeO_2.

Figure 5.13 and figure 5.14 show the imaginary part of electric modulus versus frequency plot for Al_2O_3 samples and CeO_2 samples respectively. The conductivity relaxation peaks is more clearly shown in the imaginary part of the modulus formalism versus frequency plot. The peaks shifted to higher frequencies as the conductivity increases. The existence of relaxation peaks indicate that the samples are ionic conductors (Mellander and Albinsson, 1996). No significant shift of relaxation peaks is observed for the CeO_2 samples, showing that the conductivity is not enhanced with addition of CeO_2, in agreement with the calculated conductivity values.

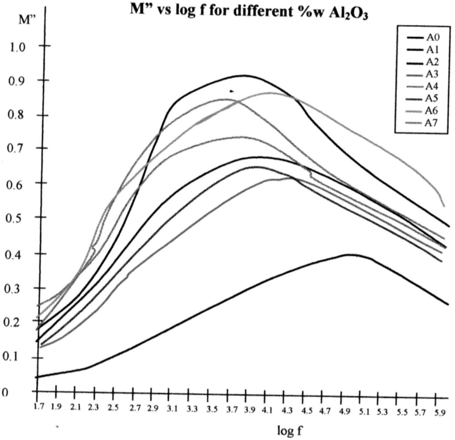

Figure 5.13 Imaginary part of electric modulus versus frequency for chitosan-lithium acetate complexes with different concentration of Al_2O_3.

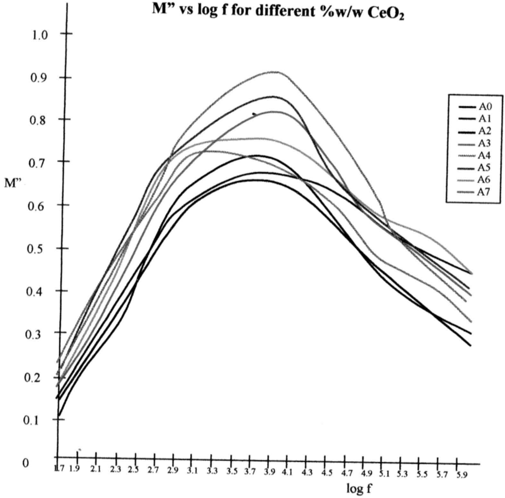

Figure 5.14 Imaginary part of electric modulus versus frequency for chitosan-lithium acetate complexes with different concentration of CeO_2.

5.4 Summary

The electrical conductivity for chitosan-lithium acetate electrolytes with added Al_2O_3 or CeO_2 as dispersoid have been calculated and presented. With Al_2O_3 added as a dispersoid, the room temperature conductivity is enhanced. However the conductivity decreases to the same order as the without dispersoid sample for the 4 wt% and above Al_2O_3 added samples. As shown by FTIR, this could be due to the less complexation occurring in these samples, thus showing that the excess of Al_2O_3 do not help in conductivity enhancement. However all CeO_2 samples show the same order in conductivity. As illustrated by FTIR, this could be due to the insignificant interaction between CeO_2 and the polymer-salt complex. Apart from interaction between dispersoids and the polymer-salt complexes, the enhancement in electrical conductivity could be attributed to the ability of the dispersoid to increase the dielectric constant of the polymer thereby making the polymer, in this case chitosan, to dissociate a greater number of salt molecules. This increases the number of mobile ions which in turn leads to the increase or enhancement in room temperature conductivity. From dielectric studies, it is shown that Al_2O_3 increases the dielectric constatnt of the material and thereby increasing the material's ability to dissociate the salt resulting in a greater number of mobile ions and lead to an increase in conductivity.