

CHAPTER 4

FTIR CHARACTERIZATION

CHAPTER 4: FTIR Characterization for complex formation

4.1 Introduction

0.8g of lithium acetate and 1g of chitosan was used as it has been proven (Yahya, 1999) to contribute for the highest room temperature electrical conductivity. The films prepared by adding different amounts of aluminium oxide or cerium oxide to chitosan-lithium acetate electrolytes appeared yellowish and opaque. They were soft and rubbery. For the films with 6 wt% and 7 wt% of aluminium oxide, precipitations were seen with naked eyes, while the same happened to films with 6 wt% and 7 wt% of added cerium oxide. This shows that the solutions were not able to assure full dispersion of the dispersoid as they were saturated. However, they were characterized for comparison in this work. It is the intention of this chapter to prove that chitosan and lithium acetate have interacted to form a complex by observing the shifts in the carbonyl, amine and NH_3^+ bands. It is also the intention of this chapter to observe the effects of adding Al_2O_3 and CeO_2 in the complex by FTIR spectroscopy.

4.2 Fourier Transformed Infrared Spectroscopy (FTIR) Analysis

FTIR spectroscopy is used for the investigation of polymer structure. The IR spectra of polymers varies with their composition. This may be able to show the interactions between various constituents and the occurrence of complexation (Jacob and Arof, 2000; Starkey and Frech, 1997; Chintapalli and Frech, 1996; Forsyth et al., 1997).

Subsequent to the observation of enhanced Li^+ - ion conductivity in LiI containing dispersions of small Al_2O_3 particles by Liang in 1973, composite solid electrolytes have been a subject of active interest in Solid State Ionics (Shukla and Sharma, 1992). $\text{LiI-Al}_2\text{O}_3$ composite was reported to exhibit about 50 times higher Li^+ -ion conductivity at room temperature in relation to the host LiI (Liang, 1973).

In the present work, FTIR spectroscopy is used to determine if there is any interaction between the polymer (chitosan), salt (lithium acetate) and dispersoid (aluminium oxide or cerium oxide). If there is interaction, it will induce changes in the vibrational modes of the molecules in the material, thus shift in wavenumbers can be observed. As the vibrational spectrum provides information through frequencies, intensities and other band properties which can be used to identify species and chemical processes, spectral studies could help to identify factors that affect the general properties and the performance of the electrolyte (Wang et al., 1996)

In this work, chitosan is used. One would expect the presence of C-O stretching at around 1100 cm^{-1} (Yun et al., 1996), the O=C-NHR band at 1650 cm^{-1} , -NH₂ and -NH₃⁺ bands at 1590 cm^{-1} and 1560 cm^{-1} respectively in the IR spectrum. If a metal ion complex with the nitrogen (N) atom, which has a lone pair electron, then the O=C-NHR, -NH₂ and -NH₃⁺ bands will shift to the vicinity of 1640 cm^{-1} , 1575 cm^{-1} and 1510 cm^{-1} (Muzzarrelli, 1978). Around 3000 cm^{-1} , the peak is due to C-H vibration. Complexation can be proven occur if these shifts are observed in the IR spectrum.

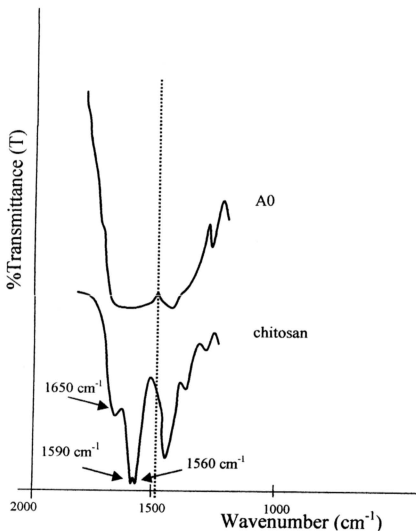


Figure 4.1. The infrared spectra of chitosan (Yahya, 1999) and chitosan-lithium acetate complex; A0 from the present work.

Figure 4.1 shows the IR spectra of a chitosan film and a chitosan film containing 0.8g LiOAc (A0) from the present work. It is observed that the chitosan film exhibit a band with 2 peaks at wavenumbers 1560 cm^{-1} and 1590 cm^{-1} . When 0.8g LiOAc was added, these peaks overlap and shifted to lower wavenumbers. This indicates that there is interaction between the chitosan and LiOAc where the salt has complexed to the lone pair electron of the nitrogen atom in chitosan. As a result of the overlapping, the chitosan-lithium salt spectrum in the region between 1640 cm^{-1} and 1510 cm^{-1} broadens and also shifted to lower wavenumbers.

In order to compare the effect of adding various wt% Al_2O_3 , the FTIR spectra are as shown in Figure 4.2.

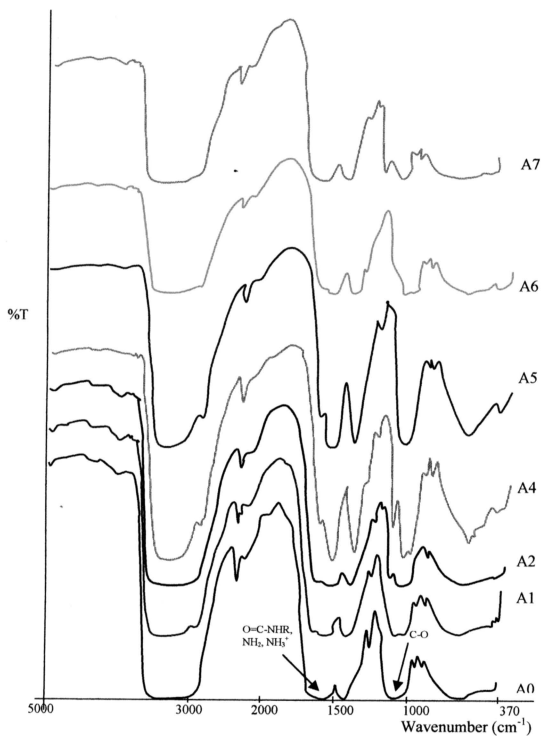


Figure 4.2. The infrared spectra of chitosan-lithium acetate complexes containing 0-7 wt% of Al_2O_3 dispersoid.

When Al_2O_3 was added, the band standing between $1000 - 1200 \text{ cm}^{-1}$ has narrowed and a shift occur at $\sim 1050 \text{ cm}^{-1}$ (see spectrum for A1). Likewise, the band between 1300 cm^{-1} to 1700 cm^{-1} has also narrowed and splits are observed at 1632 cm^{-1} and 1475 cm^{-1} (see spectrum for A1). On the whole, the spectrum is shifted lower wavenumber showing that complexation still does occur. On increase of Al_2O_3 to 2 wt%, the splitting at 1050 cm^{-1} has shifted to 1100 cm^{-1} and the splits at 1632 cm^{-1} and 1475 cm^{-1} are still observed.

At 4 wt% of Al_2O_3 added, the splitting of the band between 1300 cm^{-1} to 1700 cm^{-1} become more prominent and the split at 1100 cm^{-1} increases in intensity and another split is observed at $\sim 1050 \text{ cm}^{-1}$. It seems that the addition of Al_2O_3 prevent band overlapping but does not prevent the shifting of the spectrum to lower wavenumbers. Band broadening increases again as more Al_2O_3 was added. This can be observed in the spectra of sample, A6 and A7. This could be due to the precipitation (A6 and A7) of Al_2O_3 as it is observed that the films consist of 2 layers.

In previous work, Yahya (1999) has shown that there is interaction between chitosan and lithium acetate. The FTIR spectrum for amine group shifted to a lower wavenumber and there was an increase in the number of peaks. This shows the occurrence of complexation. For these samples, the plasticizer (EC) has been added. Compare to this work, there is no plasticizer added but dispersoid.

Figure 4.3 shows the IR spectrum of different wt% of CeO₂ added in chitosan-lithium acetate complexes as a dispersoid. This spectrum gives a wholistic idea on how the different wt% of CeO₂ added affect the vibration of the atoms in chitosan.

The effect of adding CeO₂ is not significant compared to Al₂O₃. The same case to A0, C0 shows overlapping of peaks for amine group vibrational spectrum, indicating interaction between chitosan and lithium acetate occur even without dispersoid. This has also been discussed in the beginning of this chapter. At around 1100cm⁻¹, significant shift of peaks can be seen for sample C1 to C6. The peak exhibits significant decrease in intensity with 5wt% CeO₂ and above. This might caused by the retarded in vibration due to precipitation of CeO₂ added. The same case happen to the amine peak (around 1600cm⁻¹), whereby no significant changes in the spectrum, except with 5wt% CeO₂ and above with decrease in intensity when the wt% of CeO₂ increased. Broadening of C-H vibration peak at around 3000cm⁻¹ shows the inverse effect, showing no enhancement in complexation occur for 5wt% CeO₂ and above. The spectra for C0 to C7 do not show much different. The effect of adding CeO₂ to the chitosan acetate complex does not give any significant variation. However on the whole, the spectra are shifted.

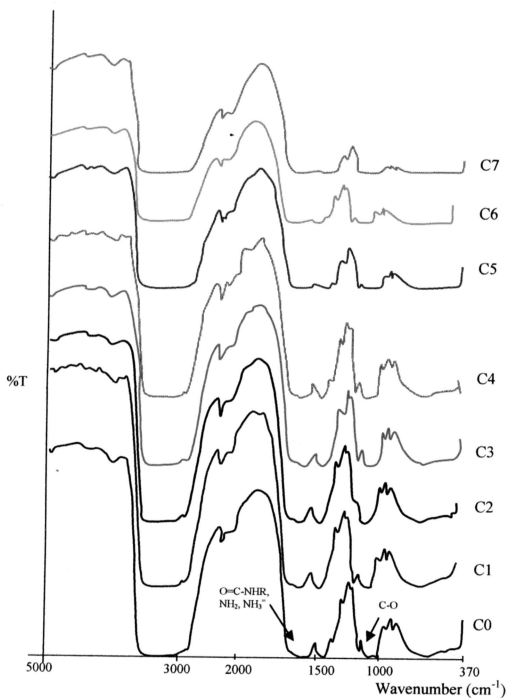


Figure 4.3. The infrared spectra of chitosan-lithium acetate complexes containing 0 - 7 wt% of CeO₂ dispersoid

4.3 Summary

It has been shown that there is interaction between chitosan and lithium acetate salt. The Al_2O_3 dispersoid has a more significant effect on the chitosan-lithium acetate complex compared to CeO_2 . Since dispersoids are known to affect the conductivity of the complexes, it is anticipated from the IR result that CeO_2 has less effect on the conductivity compared to Al_2O_3 .
