

## CHAPTER 5

### FTIR STUDIES

#### 5.1 Introduction

Fourier transform infrared spectroscopy is employed to investigate interactions between the polymers chitosan and PVA, the polymer blend and salt, the salt and plasticizer and between the plasticizer and the polymers. Many researchers [Frech and Chintapalli, 1996; Starkey and Frech, 1997; Jacob and Arof, 2000; Osman and Arof, 2003; Majid and Arof, 2005 and Hema *et al.*, 2009a] have used FTIR for this purpose. If there are any interactions, the vibrational modes of the molecules in that particular material will show shift in wave numbers.

Muzarelli *et al.*, (1977) have shown that the most important band in the FTIR spectrum to determine complexation of chitosan with metal ion is the shifting of the carboxamide and the amine bands towards lower wave numbers. Hema *et al.*, (2007, 2008, 2009a, 2009b) have shown that in PVA based polymers, the conduction takes place when the proton source from the salt hops via each coordinating site and in the case of PVA is oxygen. In PVA, the shift in the hydroxyl band to a lower wave numbers is a proof of occurrence of complexation [Rajendran *et al.*, 2003].

## 5.2 Interactions Between PVA-Chitosan

Figure 5.1 represents the FTIR region between 1490 to 1690  $\text{cm}^{-1}$  that contains the amine and carboxamide bands.

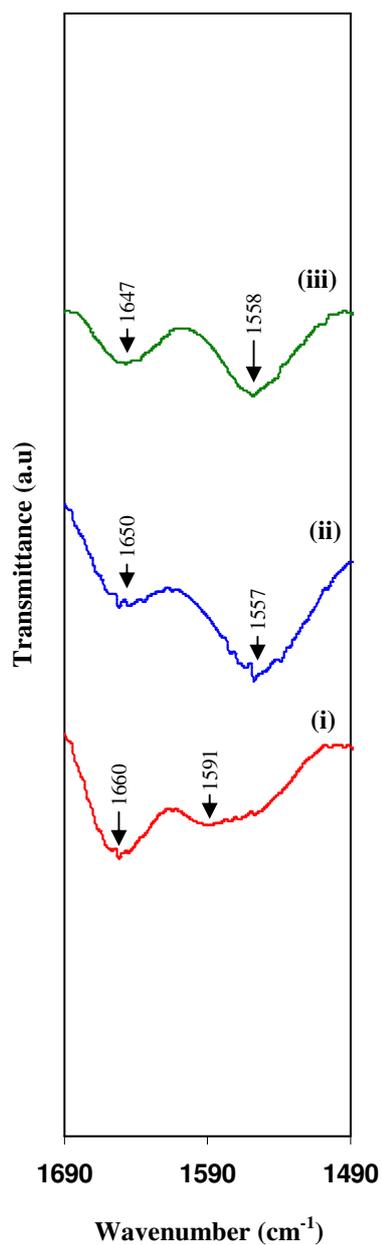


Figure 5.1: FTIR spectra of (i) pure chitosan powder, (ii) pure chitosan film and (iii) C4P6 film in the 1490 to 1690  $\text{cm}^{-1}$  spectra region.

Figure 5.2 represents the hydroxyl band in the region 3000 to 3700  $\text{cm}^{-1}$ .

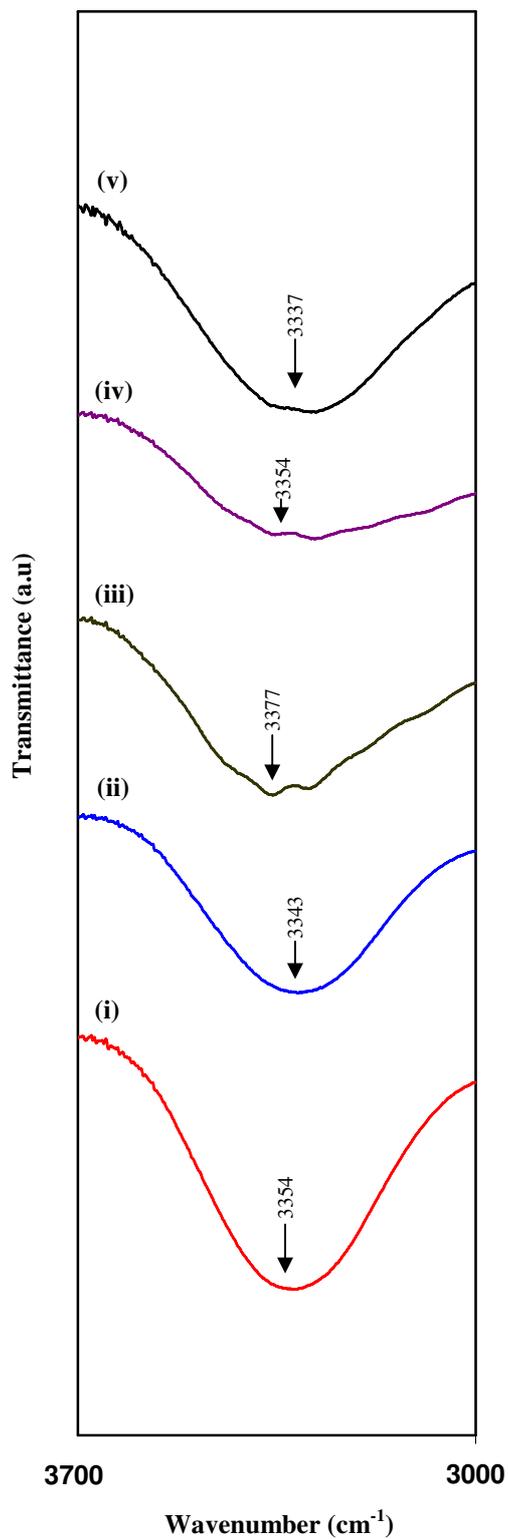


Figure 5.2: FTIR spectra of (i) pure PVA, (ii) PVA film, (iii) pure chitosan powder, (iv) pure chitosan film and (v) C4P6 film in the 3000 to 3700  $\text{cm}^{-1}$  spectra region.

From Figure 5.1 (i) it can be observed that the carboxamide (O=C-NHR) and amine (NH<sub>2</sub>) bands in the spectrum of pure chitosan powder at 1660 and 1591 cm<sup>-1</sup>, respectively. In Figure 5.1 (ii) that depicts the spectrum of the chitosan film, the carboxamide band has shifted to 1650 cm<sup>-1</sup> and the amine band to 1557 cm<sup>-1</sup>. The position of the carboxamide band for the pure chitosan film in the present work is the same as that reported by Osman and Arof, (2003). Majid and Arof, (2005) reported that the amine band in the spectrum of the pure chitosan film is situated at 1553 cm<sup>-1</sup> and their results are also comparable with the present work. The shift in these bands is attributed to interaction between the acetic acid and the nitrogen donors of chitosan polymer [Osman and Arof, 2003].

The hydroxyl band in the spectrum of pure PVA powder is shown in Figure 5.2 (i) at 3354 cm<sup>-1</sup>. The hydroxyl band in the spectrum of PVA film shown in Figure 5.2 (ii) has shifted to 3343 cm<sup>-1</sup> indicating interaction between PVA and the solvent. The hydroxyl band for chitosan powder and film is shown to peak at 3377 cm<sup>-1</sup> and 3354 cm<sup>-1</sup> in Figures 5.2 (iii) and (iv) respectively. As shown in Figure 5.2 (v), the hydroxyl band for the C4P6 film peaks at 3337 cm<sup>-1</sup>. Zhang *et al.*, (2007) suggested that the shift in peaks for the polymer blend is attributed to hydrogen bonding between hydroxyl groups in PVA and hydroxyl groups in chitosan since the hydroxyl band for the PVA-chitosan blend film shifted to lower wave numbers. Figure 5.3 is the schematic diagram of PVA and chitosan having a hydrogen bonding.

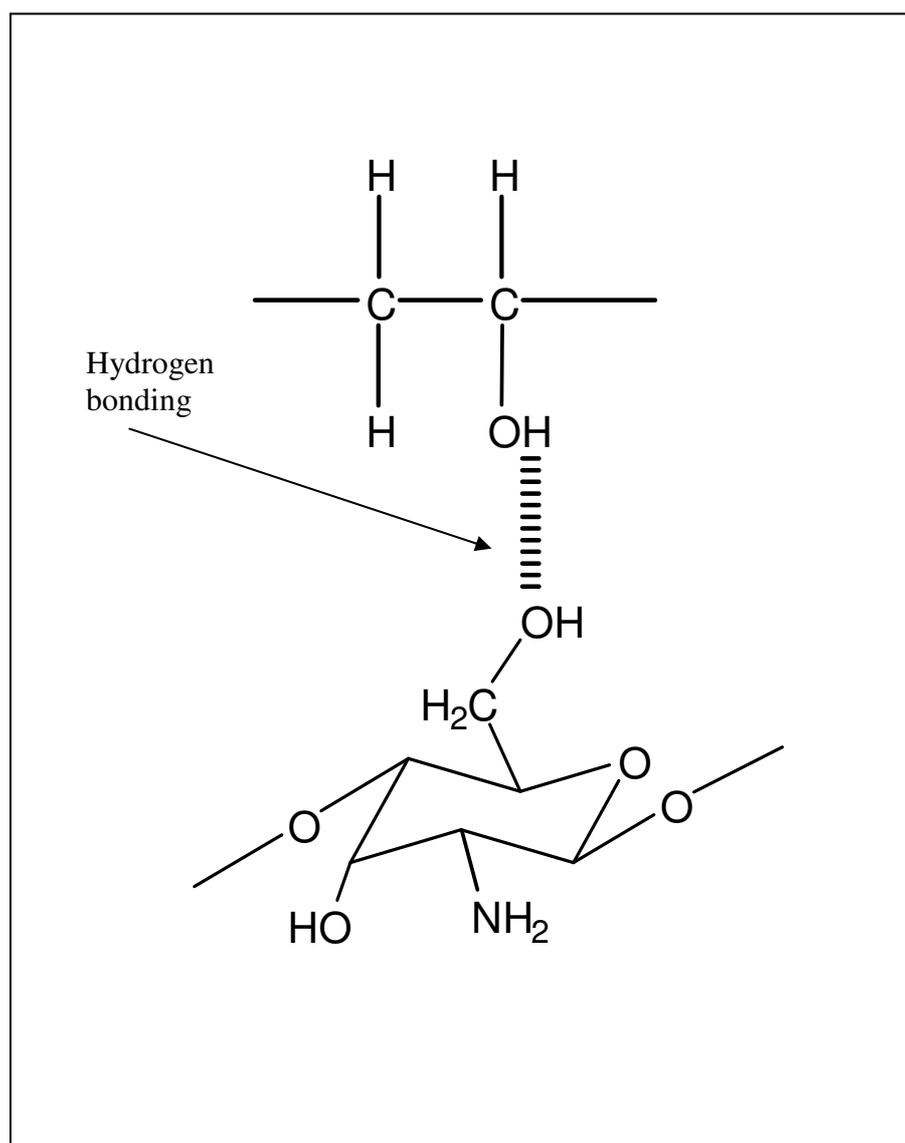


Figure 5.3: Schematic diagram of PVA-chitosan blend having a hydrogen bonding.

### 5.3 Interactions between Chitosan-NH<sub>4</sub>NO<sub>3</sub>

Figure 5.4 depicts the FTIR spectra of the 90 wt.% chitosan-10 wt.% NH<sub>4</sub>NO<sub>3</sub>, 70 wt.% chitosan-30 wt.% NH<sub>4</sub>NO<sub>3</sub> and 50 wt.% chitosan-50 wt.% NH<sub>4</sub>NO<sub>3</sub> electrolytes in the region 3000 to 3700 cm<sup>-1</sup>.

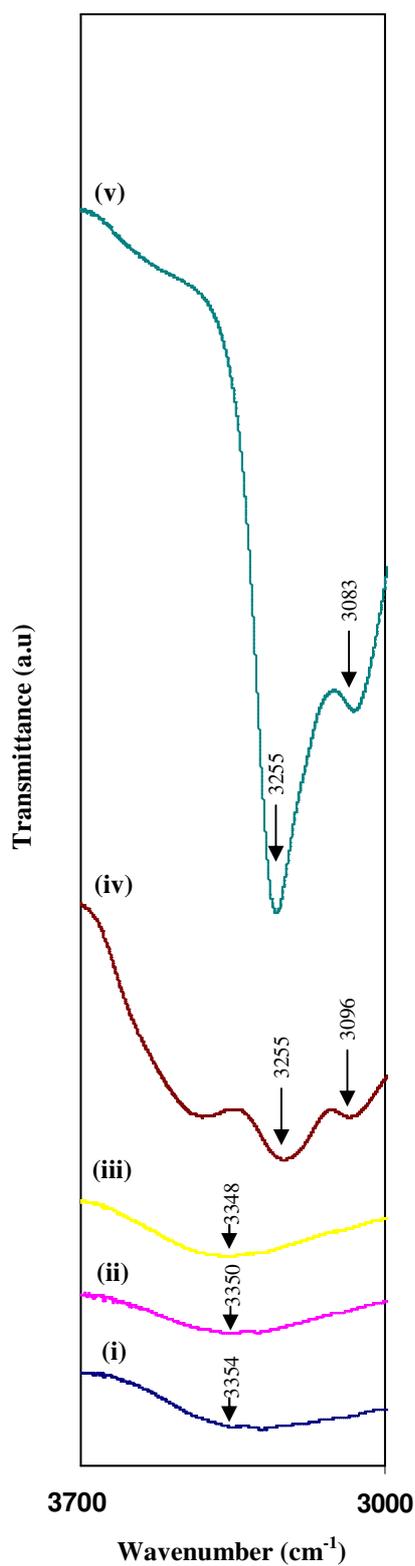


Figure 5.4: FTIR spectra of (i) pure chitosan film and pure chitosan film with (ii) 10 wt. %  $\text{NH}_4\text{NO}_3$ , (iii) 30 wt. %  $\text{NH}_4\text{NO}_3$ , (iv) 50 wt. %  $\text{NH}_4\text{NO}_3$  and (v) pure  $\text{NH}_4\text{NO}_3$  salt in the 3000 to 3700  $\text{cm}^{-1}$  spectra region.

From Figure 5.4 (ii) and (iii), addition of 10 and 30 wt.%  $\text{NH}_4\text{NO}_3$ , the hydroxyl band has down shifted to lower wavenumbers from 3354 to 3350 and 3348  $\text{cm}^{-1}$  respectively. These shifts proved that there is interaction between the salt and the OH group in chitosan. New peaks at 3255 and 3096  $\text{cm}^{-1}$  appeared in the spectra for the sample with 50 wt.%  $\text{NH}_4\text{NO}_3$  salt, Figure 5.4 (iv) is due to  $\nu(\text{N-H})$  stretching of  $\text{NH}_4\text{NO}_3$ . This indicates that more  $\text{NH}_4\text{NO}_3$  aggregates have formed that will limit the conduction of ions. Figure 5.5 is the schematic diagram of a chitosan having an interaction with  $\text{NH}_4\text{NO}_3$  salt at hydroxyl group.

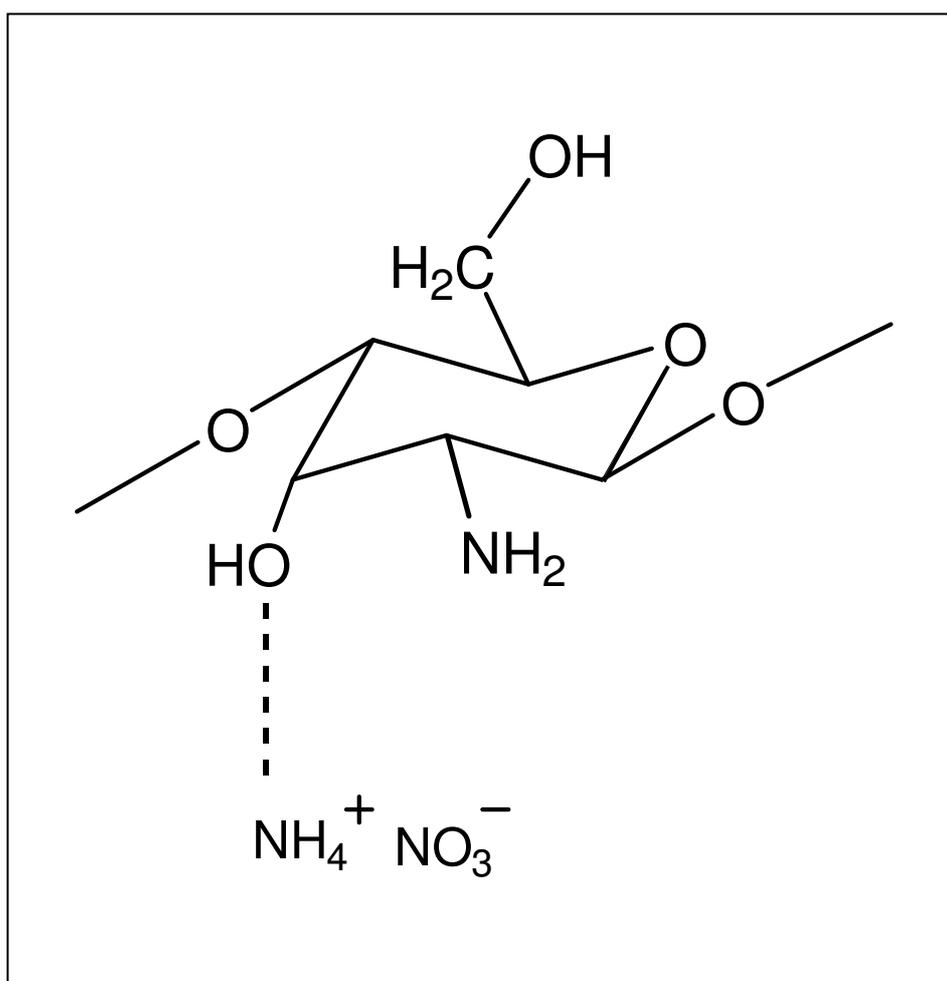


Figure 5.5: Schematic diagram of chitosan having interaction with  $\text{NH}_4\text{NO}_3$  at hydroxyl group.

Figure 5.6 depicts the FTIR spectrum for chitosan-NH<sub>4</sub>NO<sub>3</sub> electrolytes with different salt contents in the region 1490 to 1700 cm<sup>-1</sup>.

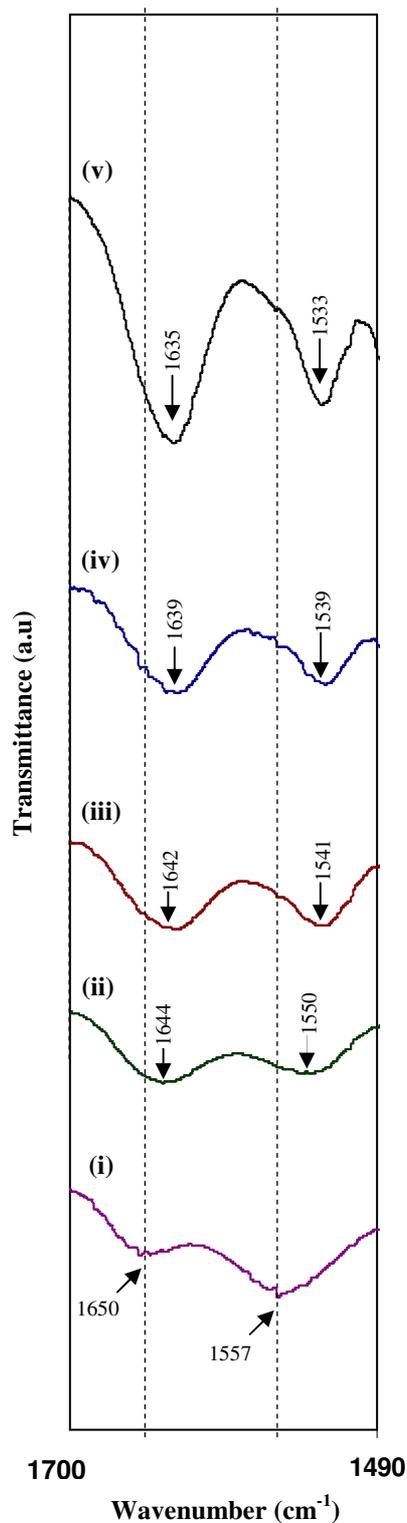


Figure 5.6: FTIR spectra of (i) pure chitosan film and chitosan with (ii) 20 wt.% NH<sub>4</sub>NO<sub>3</sub>, (iii) 30 wt.% NH<sub>4</sub>NO<sub>3</sub>, (iv) 40 wt.% NH<sub>4</sub>NO<sub>3</sub> and (v) 50 wt.% NH<sub>4</sub>NO<sub>3</sub> in the 1490 to 1700 cm<sup>-1</sup> spectra region.

The amine band of pure chitosan film appears at  $1557\text{ cm}^{-1}$  and the carboxamide band at  $1650\text{ cm}^{-1}$ , Figure 5.6 (i). On addition of 20 wt.%  $\text{NH}_4\text{NO}_3$  salt, Figure 5.6 (ii) the carboxamide and amine bands have shifted to  $1644$  and  $1550\text{ cm}^{-1}$ . The bands shift to even lower wavenumbers on addition of 30, 40 and 50 wt.% of  $\text{NH}_4\text{NO}_3$ , Figure 5.6 (iii) to (v). This indicates that complexation may also occur at the amino group as have been reported by Majid and Arof, (2005). Hashmi *et al.*, (1990) have proven that for PEO- $\text{NH}_4\text{ClO}_4$  system, the conducting species of the complex is the  $\text{H}^+$  ion which originates from the ammonium ion and the conduction occurs via the Grotthus mechanism.

Buraidah *et al.*, (2009) have concluded that in the chitosan- $\text{NH}_4\text{I}$  complex the cations from  $\text{NH}_4\text{I}$  coordinates with the N atom of the amino group in chitosan. Hence from FTIR spectroscopy, the interaction between chitosan and  $\text{NH}_4\text{NO}_3$  has been confirmed and the conduction mechanism in the polymer electrolytes is expected to occur via the Grotthus mechanism. Complexation at  $\text{NH}_2$  group may occur as depicted in Figure 5.7.

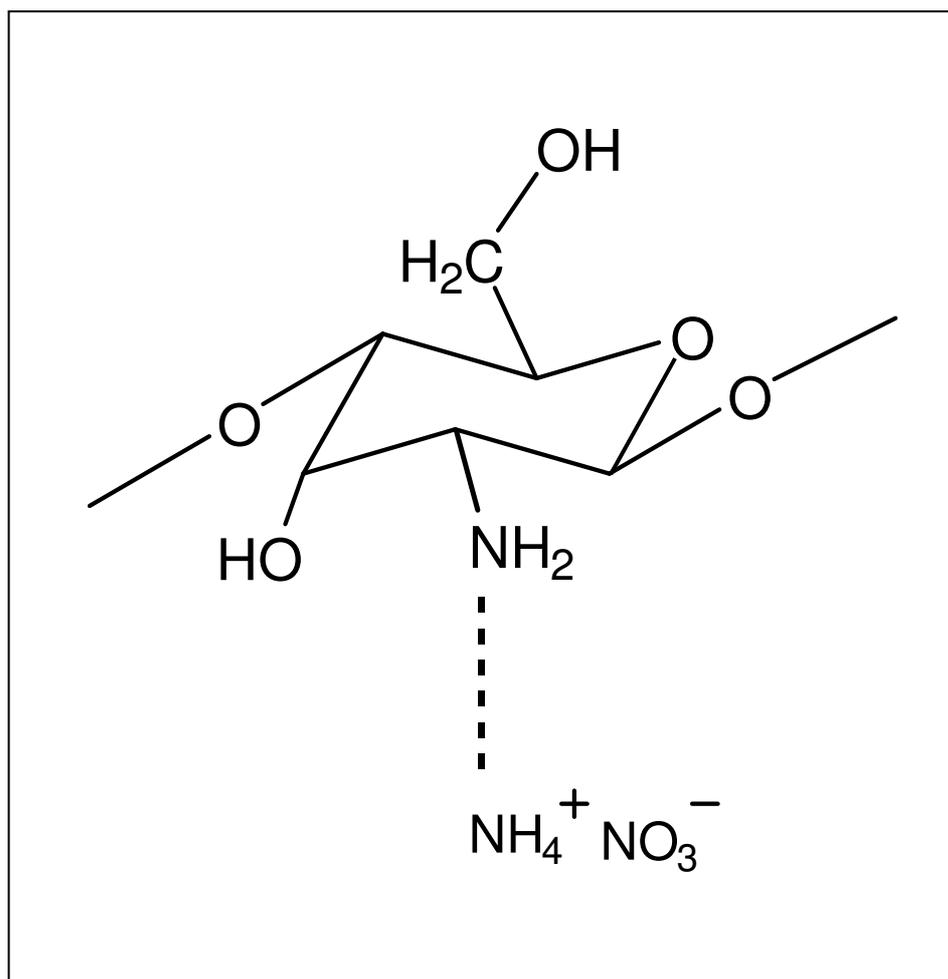
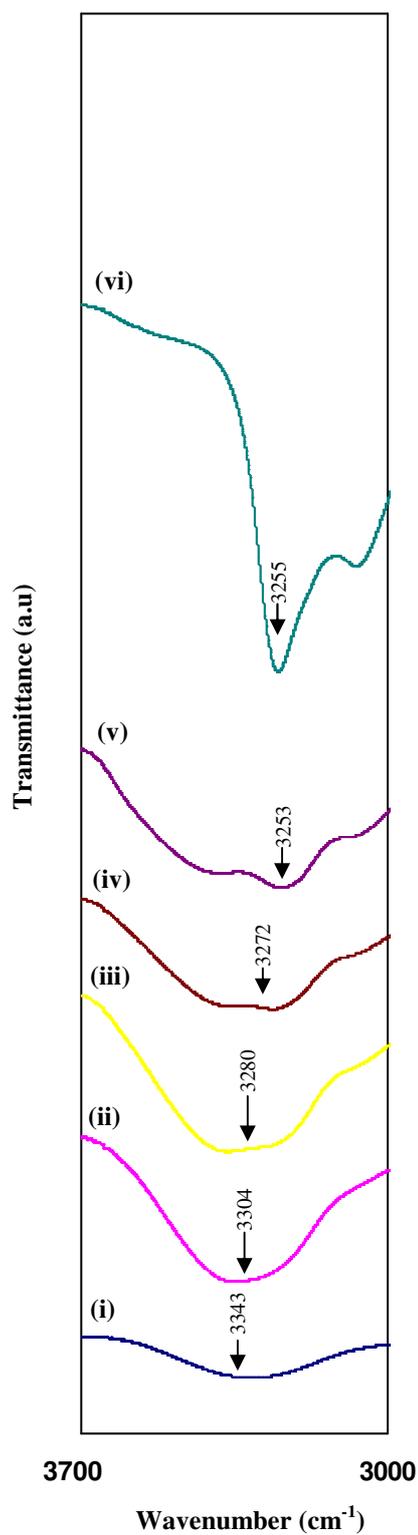


Figure 5.7: Schematic diagram of complexation between amine group in chitosan with  $\text{NH}_4\text{NO}_3$  salt.

#### 5.4 Interactions Between PVA- $\text{NH}_4\text{NO}_3$

Figure 5.8 presents the FTIR spectra of PVA- $\text{NH}_4\text{NO}_3$  films with 10 to 50 wt.%  $\text{NH}_4\text{NO}_3$  in the range from 3700 to 3000  $\text{cm}^{-1}$ .



**Figure 5.8:** FTIR spectra of (i) pure PVA film and PVA with (ii) 10 wt.% NH<sub>4</sub>NO<sub>3</sub>, (iii) 20 wt.% NH<sub>4</sub>NO<sub>3</sub>, (iv) 30 wt.% NH<sub>4</sub>NO<sub>3</sub>, (v) 50 wt.% NH<sub>4</sub>NO<sub>3</sub> and (vi) pure NH<sub>4</sub>NO<sub>3</sub> salt in the 3000 to 3700 cm<sup>-1</sup> spectra region.

In the present work the stretching vibration of hydroxyl group ( $\nu\text{OH}$ ) band of pure PVA film appears at the  $3343\text{ cm}^{-1}$  Figure 5.8 (i). On addition of 30 wt.%  $\text{NH}_4\text{NO}_3$  salt, the band shifts to lower wavenumbers at  $3272\text{ cm}^{-1}$ , Figure 5.8 (iv). The appearance of peak at  $3253\text{ cm}^{-1}$ , Figure 5.8 (v) is attributable to  $\nu(\text{N-H})$  stretching of  $\text{NH}_4\text{NO}_3$  as depicted in Figure 5.8 (vi) that results in  $\text{NH}_4\text{NO}_3$  aggregates formation. Hema *et al.*, (2008) have reported that in PVA- $\text{NH}_4\text{Br}$  complex system the conduction also occurs via the O-H group following the Grotthus mechanism on the addition of 10 % mol of  $\text{NH}_4\text{Br}$ . A similar explanation was given for the PVA- $\text{NH}_4\text{I}$  system [Hema *et al.*, 2009a]. This shows that the salt can also complex with the hydroxyl group that may take place as shown in Figure 5.9.

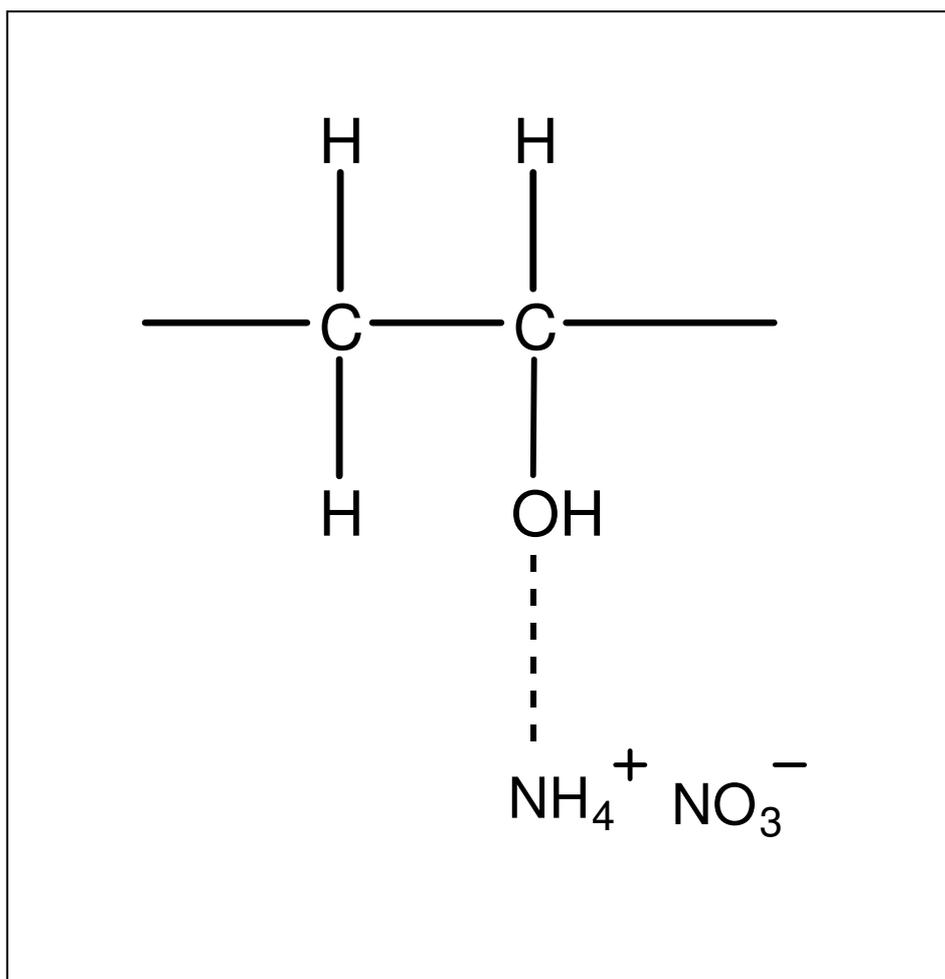
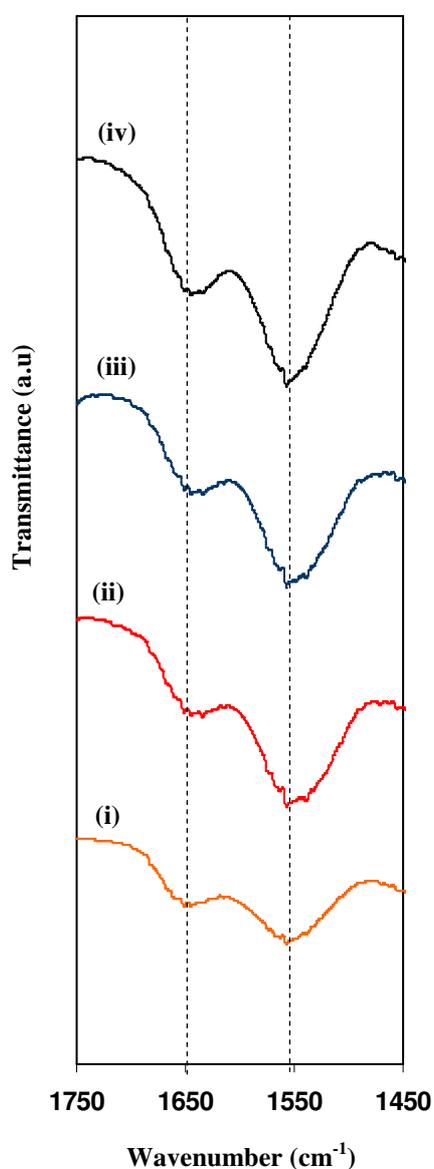


Figure 5.9: Schematic diagram of complexation between OH group in PVA with  $\text{NH}_4\text{NO}_3$  salt.

## 5.5 Interactions Between Chitosan-EC

Figure 5.10 represents the spectra in the region of amine and carboxamide bands for chitosan-EC films. From the spectra, it is observed that the shift in peaks of the two bands is hardly noticeable. The present results are comparable with Osman and Arof, (2003) where it can be concluded that there are no interactions between pure chitosan film and ethylene carbonate.



**Figure 5.10:** FTIR spectra of (i) pure chitosan film and chitosan with (ii) 10 wt.% EC, (iii) 30 wt.% EC and (iv) 50 wt.% EC in the 1450 to 1750 cm<sup>-1</sup> spectra region.

Figure 5.11 presents the hydroxyl band for chitosan-EC interaction. It is noticed that on addition of 10, 30 and 50 wt.% of EC no shift of bands occurred hence there are no complexation between chitosan and EC.

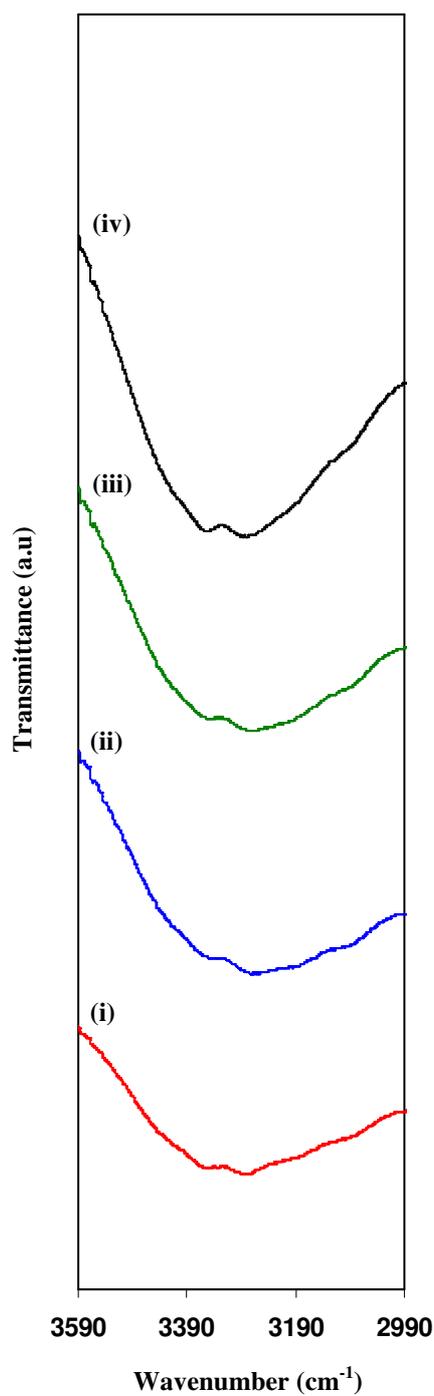
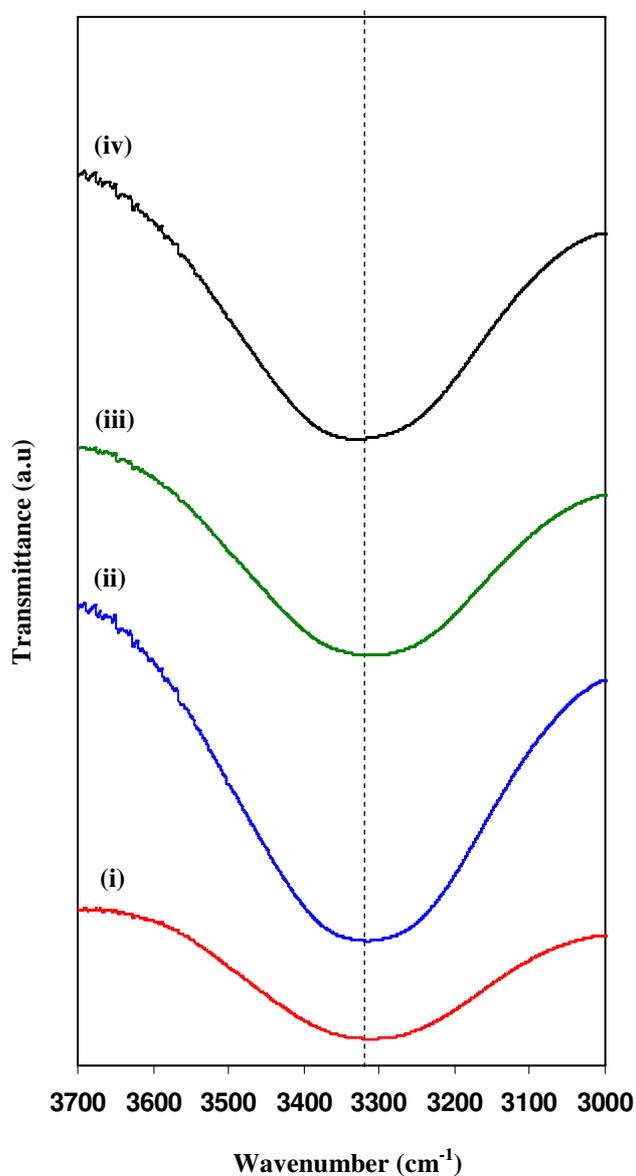


Figure 5.11: FTIR spectra of (i) pure chitosan film and chitosan with (ii) 10 wt.% EC, (iii) 30 wt.% EC and (iv) 50 wt.% EC in the 2990 to 3590 cm<sup>-1</sup> spectra region.

## 5.6 Interactions Between PVA-EC

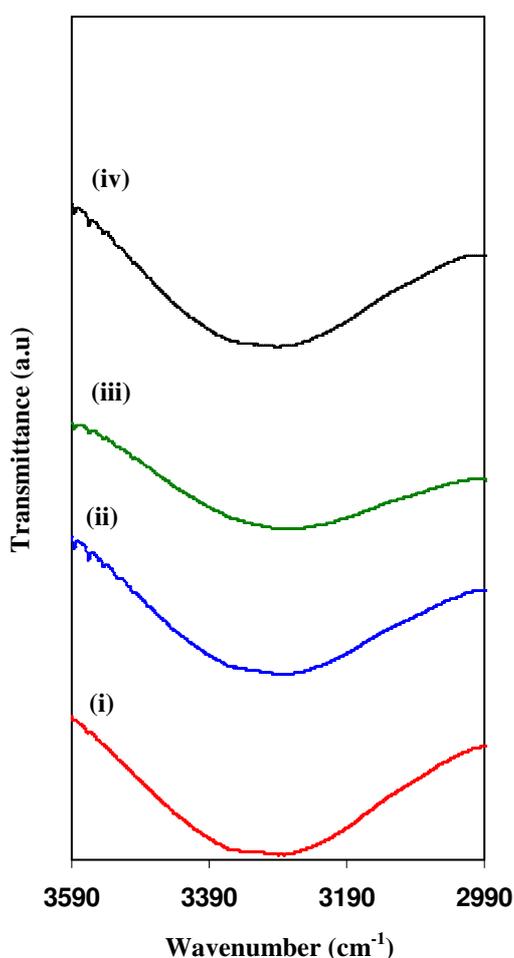
Figure 5.12 represents the infrared spectra of pure PVA film and PVA with the addition of 10, 30 and 50 wt.% EC in the region of the hydroxyl band. From the spectra in Figure 5.12, it is observed that the OH band in the spectrum of the pure PVA film did not exhibit any significant shift.



**Figure 5.12:** FTIR spectra of (i) pure PVA film and PVA with (ii) 10 wt.% EC, (iii) 30 wt.% EC (iv) and 50 wt.% EC in the 3000 to 3700 cm<sup>-1</sup> spectra region.

## 5.7 Interactions Between PVA-Chitosan-EC

Figure 5.13 represents the FTIR spectra of pure PVA-chitosan blend and that of the blend plasticized with 10, 30 and 50 wt.% EC in the region 2990 to 3590  $\text{cm}^{-1}$ . It can be inferred that EC does not interact with the polymer blend but merely serves as a lubricant to the blend. However the hydroxyl band in the C4P6 is significantly different from the position of the hydroxyl band in pure chitosan and PVA. This has been attributed to the formation of hydrogen bonds between the OH groups in chitosan and PVA.



**Figure 5.13:** FTIR spectra of (i) C4P6 and C4P6 with (ii) 10 wt.% EC, (iii) 30 wt.% EC and (iv) 50 wt.% EC in the 2990 to 3590  $\text{cm}^{-1}$  spectra region.

Figure 5.14 represents the FTIR spectra for the unplasticized and plasticized polymer blends in the region from 1505 to 1685  $\text{cm}^{-1}$ . Again EC can be said to act as diluent to the blend. The plasticizer can be said to be dispersed in the C4P6 polymer blend host.

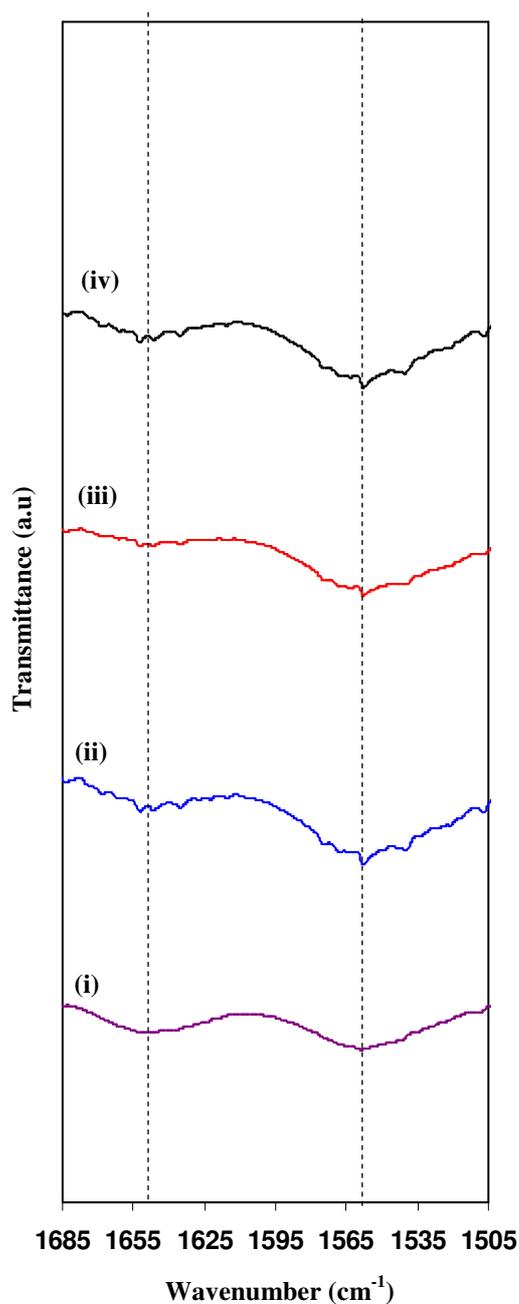
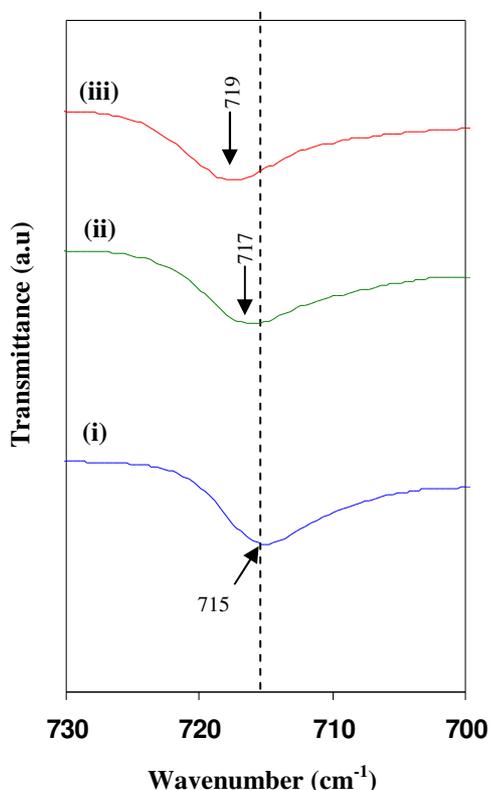


Figure 5.14: FTIR spectra of (i) C4P6 and C4P6 with (ii) 10 wt.% EC, (iii) 30 wt.% EC and (iv) 50 wt.% EC in the 1505 to 1685  $\text{cm}^{-1}$  spectra region.

## 5.8 Interactions Between $\text{NH}_4\text{NO}_3$ -EC

In a plasticized system, it is important to determine if there is interaction between the salt and the plasticizer. If there is, then interaction should occur between cation of the salt (in this case  $\text{NH}_4^+$ ) and the carbonyl group ( $\text{C}=\text{O}$ ) of plasticizer (EC). Figure 5.15 shows the FTIR spectra of EC and EC mixed with different weight ratios of  $\text{NH}_4\text{NO}_3$ . The  $\text{C}=\text{O}$  bending band has shifted from 715 to 719  $\text{cm}^{-1}$ . The interaction between the  $\text{NH}_4^+$  ion and the oxygen atom is only a weak interaction and the cation can be removed when it collides with another cations when it has enough activation energy for migration. In the work of Osman and Arof, (2003) the shift of the  $\text{C}=\text{O}$  bending band in pure EC was reportedly due to the interaction between  $\text{Li}^+$  salt and  $\text{C}=\text{O}$  group of the EC molecule and their results were in good agreement with Chintapalli and Frech, (1996).



**Figure 5.15:** FTIR spectra of (i) pure EC, (ii) EC mixed with 0.5 wt.%  $\text{NH}_4\text{NO}_3$  and (iii) EC mixed with 1.1 wt.%  $\text{NH}_4\text{NO}_3$  in the region of  $\text{C}=\text{O}$  bending band.

Figure 5.16 shows the shift in the C=O stretching bands. This shift confirms interaction between EC and the salt.

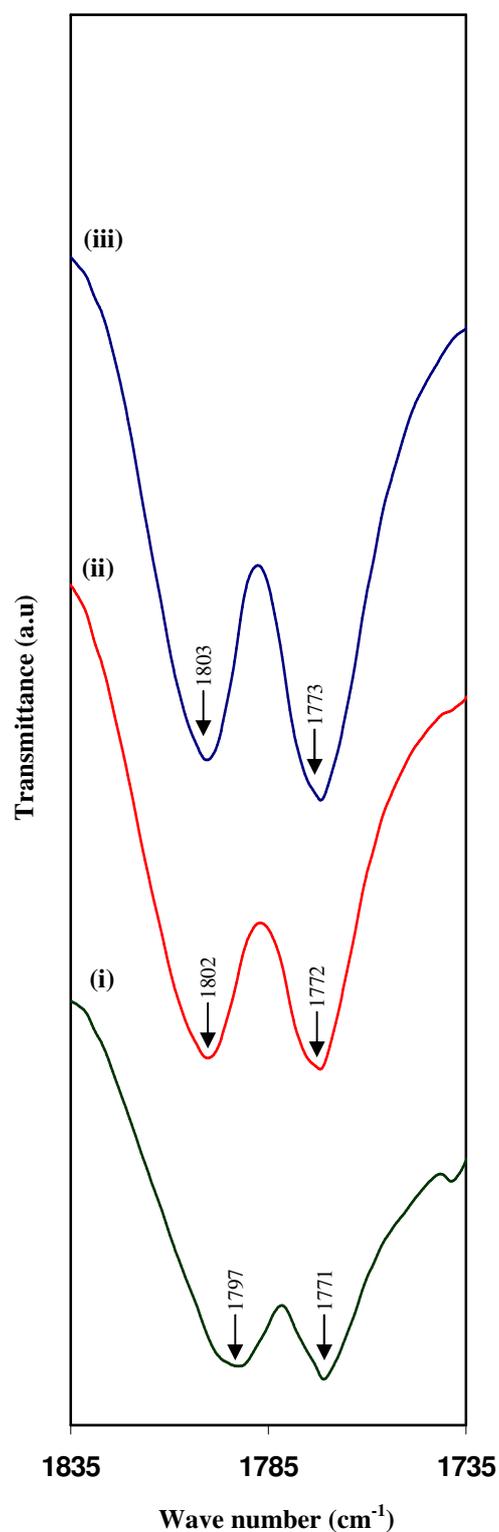
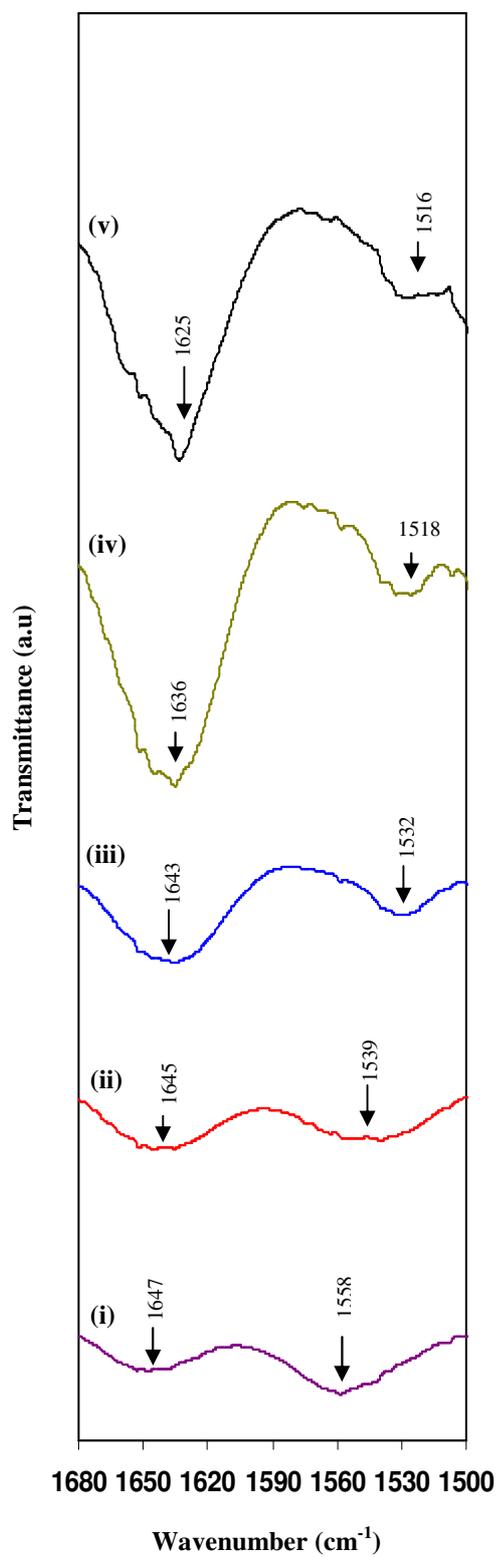


Figure 5.16: FTIR spectra of (i) pure EC, (ii) EC mixed with 0.5 wt.% of NH<sub>4</sub>NO<sub>3</sub> and (iii) EC mixed with 1.1 wt.% of NH<sub>4</sub>NO<sub>3</sub> in the region of C=O stretching band.

In the present study it can be inferred that the  $H^+$  from the cation of the salt has interacted (formed a weak bond) with the carbonyl  $C=O$  band of EC molecule since the  $C=O$  bending band has shifted when  $NH_4NO_3$  was added. The doublet bands in Figure 5.16 represents vibrations of  $C=O$  stretching. In pure EC, the doublet bands are observed at 1771 and 1797  $cm^{-1}$ . With the addition of 0.5 wt.%  $NH_4NO_3$ , the bands shifted to 1772 and 1802  $cm^{-1}$ . After the addition of 1.1 wt.% of salt, the bands have shifted to 1773 and 1803  $cm^{-1}$ . The shifts that occurred in this doublet band are in agreement with that reported by Osman and Arof, (2003) and infers interaction between salt and EC.

### 5.9 Interactions Between PVA-Chitosan- $NH_4NO_3$ (Salted System)

In the present work the amine band of C4P6 film appears at the 1558  $cm^{-1}$  and the carboxamide band at 1647  $cm^{-1}$ , Figure 5.17 (i). On addition of 10 wt. % of  $NH_4NO_3$  salt (90[C4P6]-10AN), Figure 5.17 (ii) the carboxamide and amine bands have shifted to 1645 and 1539  $cm^{-1}$ . On addition of 50 wt. %  $NH_4NO_3$  (50[C4P6]-50AN) the peaks for carboxamide and amine bands shifted to 1625 and 1516  $cm^{-1}$  respectively, Figure 5.17 (v). These results show that the salt has complexed with the polymer blend.



**Figure 5.17:** FTIR spectra for (i) C4P6, (ii) 90[C4P6]-10AN, (iii) 80[C4P6]-20AN, (iv) 60[C4P6]-40AN and (v) 50[C4P6]-50AN in the 1500 to 1680 cm<sup>-1</sup> spectra region.

Figure 5.18 depicts the FTIR results in the hydroxyl region for C4P6 doped with 10, 20, 40 and 50 wt.%  $\text{NH}_4\text{NO}_3$ . The addition of 40 wt.%  $\text{NH}_4\text{NO}_3$  salt has shifted the hydroxyl band to lower wavenumbers from 3337 to 3318  $\text{cm}^{-1}$ , Figure 5.18 (iv). The NH band becomes more obvious as the amount of salt increased and this is most distinctly observed in Figure 5.18 (v). This could be a possible reason that the conductivity of the salted system decreased after addition of more than 40 wt.%  $\text{NH}_4\text{NO}_3$  salt. The shift in the carboxamide, amine and hydroxyl bands indicates that interaction occurred between the PVA-chitosan blend (host) and  $\text{NH}_4\text{NO}_3$  (doping salt).

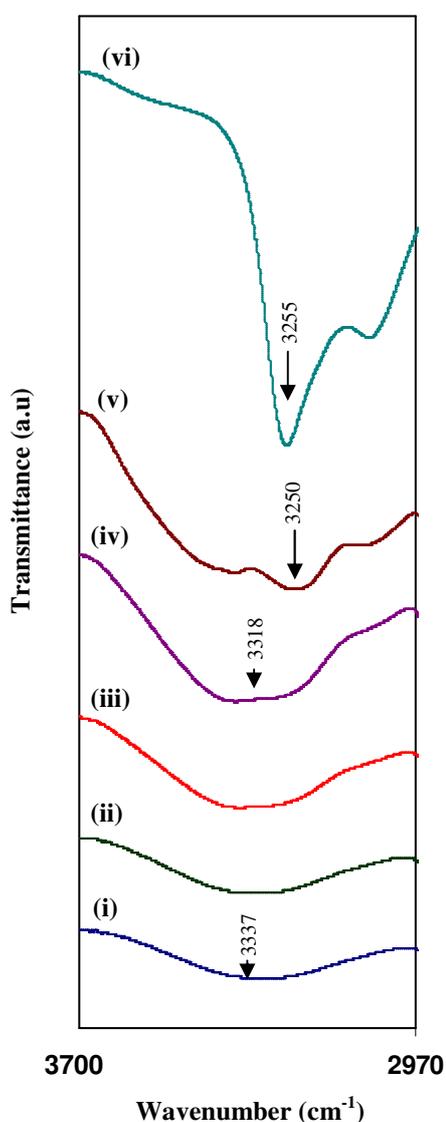


Figure 5.18: FTIR spectra for (i) C4P6 (ii) 90[C4P6]-10AN, (iii) 80[C4P6]-20AN, (iv) 60[C4P6]-40AN, (v) 50[C4P6]-50AN and (vi) pure  $\text{NH}_4\text{NO}_3$  in the 2970 to 3700  $\text{cm}^{-1}$  spectra region.

From the FTIR results, the interaction between PVA-chitosan blend and  $\text{NH}_4\text{NO}_3$  salt can be proposed as depicted in Figure 5.19.

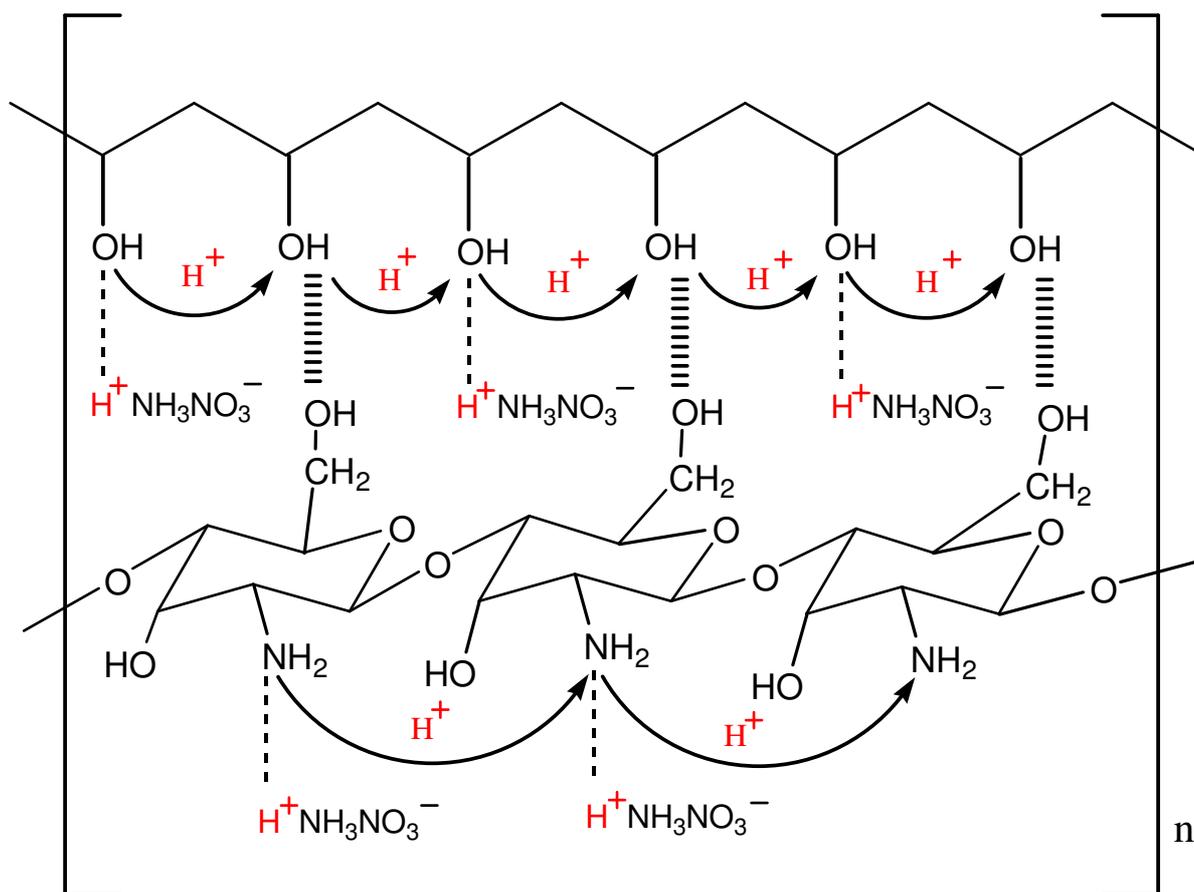


Figure 5.19:  $\text{H}^+$  conduction mechanism in salted system.

### 5.10 Interactions Between PVA-Chitosan- $\text{NH}_4\text{NO}_3$ -EC (Plasticized System)

No peak is expected in the spectrum of 60[C4P6]-40AN film in the region of carbonyl bending. The shifts observed in Figure 5.20 (ii) and (iii) are due to the interaction between  $\text{NH}_4^+$  and the oxygen atom in the carbonyl group.

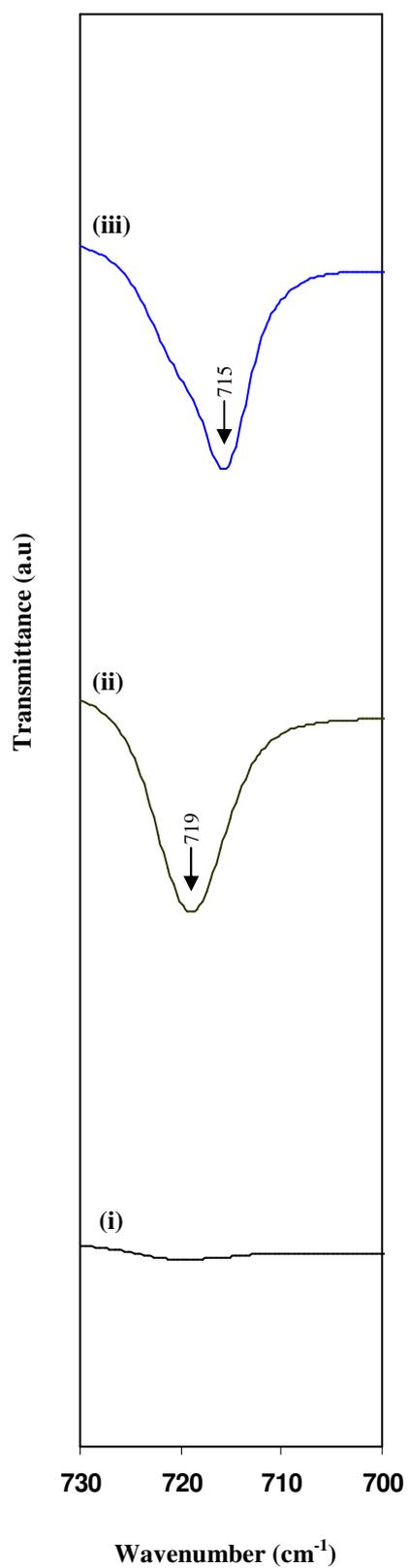
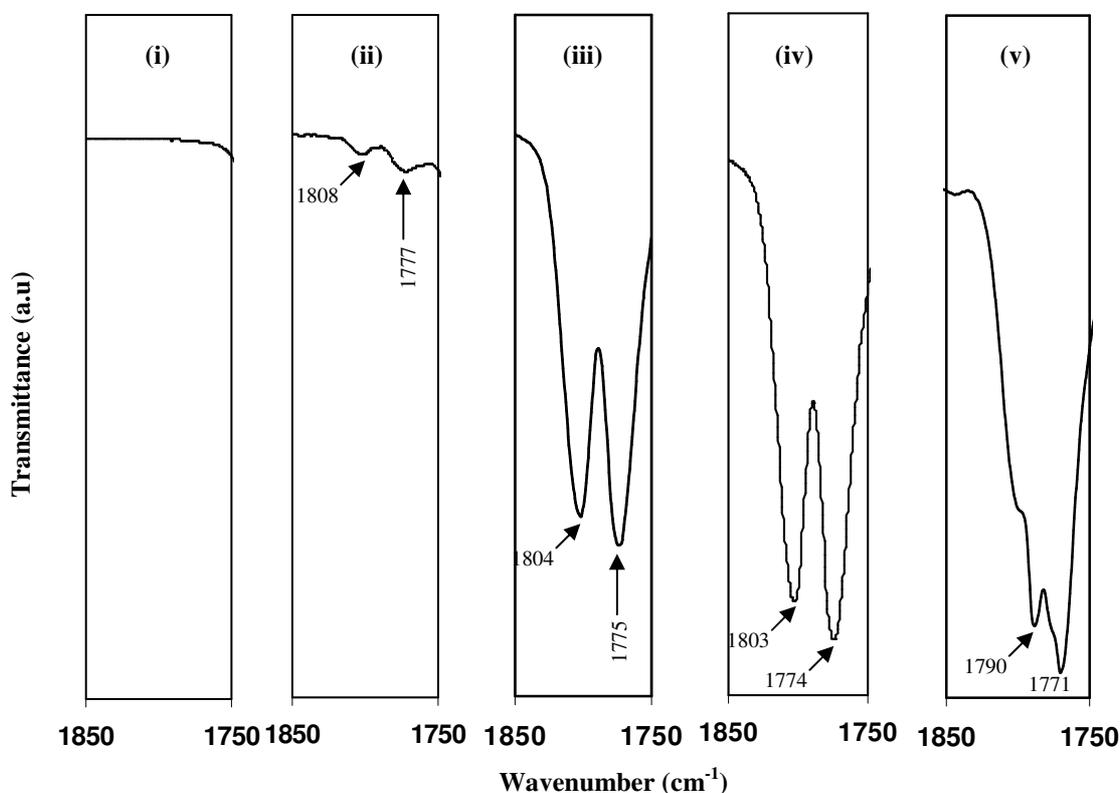


Figure 5.20: FTIR spectra for (i) 60[C4P6]-40AN, (ii) 30[60C4P6-40AN]-70EC and (iii) 20[60C4P6-40AN]-80EC in the region of C=O bending band.

Figure 5.21 shows the FTIR results for PVA-chitosan-NH<sub>4</sub>NO<sub>3</sub>-EC system in the stretching mode of the carbonyl band.



**Figure 5.21:** FTIR spectra for (i) 60[C4P6]-40AN, (ii) 60[60C4P6-40AN]-40EC, (iii) 40[60C4P6-40AN]-60EC, (iv) 30[60C4P6-40AN]-70EC and (v) 20[60C4P6-40AN]-80EC in the region of C=O stretching band.

From Figure 5.21 (i) no doublet C=O stretching of EC is observed in the spectrum of 0 wt.% EC (60[C4P6]-40AN). With addition of 40 wt.% EC (60[C4P6-40AN]-40EC), a C=O doublet peak was observed at 1777 and 1808 cm<sup>-1</sup>, Figure 5.21 (ii). The doublet peaks shifted to even lower wavenumbers on the addition of 60 wt. % EC (40[60C4P6-40AN]-60EC). Further addition of 70 wt.% EC (30[60C4P6-40AN]-70EC) has shifted the doublet peaks down shifted further to 1774 and 1803 cm<sup>-1</sup>, Figure 5.21 (iv). On addition of 80 wt.% of EC (20[60C4P6-40AN]-80EC), the doublet peak has shifted to 1771 and 1790 cm<sup>-1</sup> and the intensity of the peak has also decreased, Figure 5.21 (v).

Figure 5.22 shows the  $H^+$  conduction mechanism in plasticized system in the present work. It may be expected that the activation energy of the plasticized sample has reduced due to the shorter distance of transit site available.

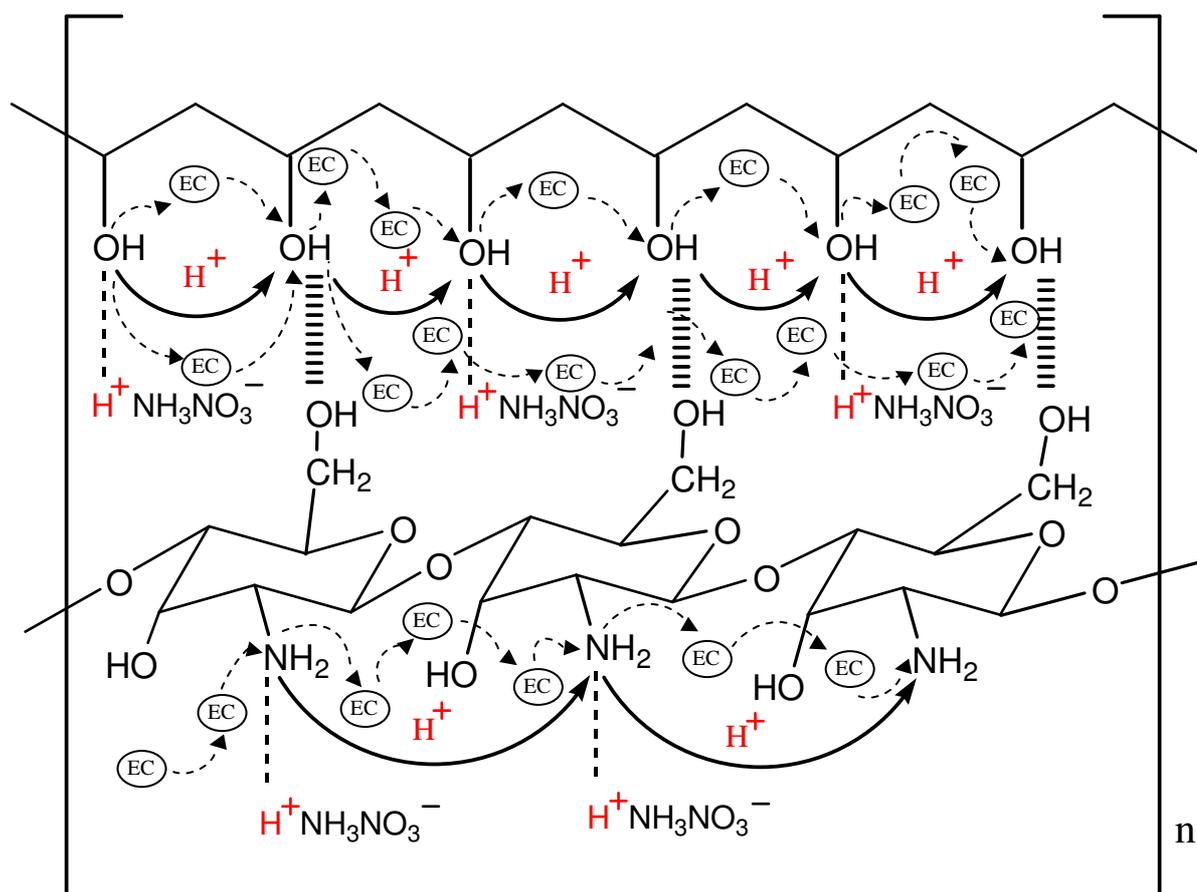


Figure 5.22:  $H^+$  conduction mechanism in plasticized system.

-  Original hopping without plasticizer
-  New pathways (with plasticizer) resulting in lower activation energy.

### 5.11 Summary

From FTIR studies, the PVA film has a hydroxyl group and chitosan film has amine, carboxamide and hydroxyl groups. The blend of PVA and chitosan therefore has carboxamide, amine and hydroxyl groups. The ammonium nitrate salt has interacted with chitosan at the carboxamide, amine and hydroxyl groups since the bands have shifted. The hydroxyl band in PVA film also shifts indicating complexation with  $\text{NH}_4\text{NO}_3$  salt. The PVA-chitosan blend has also interacted with the  $\text{NH}_4\text{NO}_3$  salt when the carboxamide, amine and hydroxyl bands shift to lower wave numbers. From FTIR results, there is no interaction between the PVA-EC since the hydroxyl band did not show any shift. For chitosan-EC, the carboxamide, amine and hydroxyl bands also did not shift indicating that chitosan and EC did not interact. The PVA-chitosan blend also did not interact with the plasticizer. However it is observed that interaction occurs between the salt and EC where it is noticeable that the C=O bending and C=O stretching bands have shifted. Interaction between  $\text{NH}_4\text{NO}_3$  and EC in PVA-chitosan- $\text{NH}_4\text{NO}_3$ -EC systems has been confirmed since the C=O stretching and C=O bending bands have shifted.