

CHAPTER 6**INFRARED STUDIES OF CHITOSAN-NH₄SCN COMPLEXES AND
CHITOSAN-NH₄SCN-Al₂TiO₅ COMPOSITE****6.1 Introduction**

Since Liang (1973) reported that ionic conductivity of LiI can be increased significantly by the addition of insulating alumina particles, efforts have been taken theoretically and experimentally to understand the mechanism of this effect and to transfer it to other ionic conducting systems [Maier, 1986; Stoneham et al., 1979]. Ionic conductors with filler added are called “composites”.

Theoretically, for composites containing insulating oxides an increase of the ionic conductivity is expected which is generally explained by the formation of space charge layers at the matrix-particle interfaces where a concentration profile of charge carriers exist (even in equilibrium state). The increase in conductivity is due to the formation of excess vacancies [Jow et al., 1979; Maier, 1986]. On the other hand, the lowering of electrical conductivity for composites containing high contents of insulating particles is due to blocking effects.

The field of polymer electrolytes has developed along three stages: dry solid systems, polymer gels, and polymer composites. The addition of inert oxides to the polymer electrolytes has become an attractive approach, due to the improved mechanical stability and enhanced ionic conductivity [Wieczorek et al., 1996; Croce et

al., 1998]. It has been shown that the addition of ceramic filler improves the conductivity of poly(ethylene oxide) (PEO)-based polymer electrolyte as well as the interfacial resistance between the electrolyte and electrode [Leo et al., 2002].

Further studies reported that the addition of Al_2O_3 [Ahn et al., 2003; Dissanayake et al., 2003], TiO_2 [Best et al., 1999], BaTiO_3 [Sun et al., 2000] and other fillers such as SiO_2 and related oxides [Shin et al., 2005] to polyethyleneoxide (PEO)-based polymeric electrolytes improved the ionic conductivity. Mechanisms of such conductivity enhancement have also been studied by impedance spectroscopy and NMR measurements [Tambelli et al., 2002; Singh et al., 2004].

The objective of this chapter is to study interactions between chitosan, NH_4SCN and Al_2TiO_5 in the polymer-salt complex and composite electrolyte.

6.2 The FTIR spectrum of chitosan- Al_2TiO_5

The utilization of fourier transform infrared (FTIR) spectroscopic technique to identify the component materials and study their interactions is well accepted. The interaction can be identified through changes in intensity, bandwidth and position of bands in the IR spectrum [Deepa et al., 2004].

It is important to show that complexation occurs between the polymer host and the filler. FTIR is an important tool in the investigation of polymer structure. Since in the present investigation, other than salt, fillers are also added to the polymer with the aim of enhancing electrical conductivity and mechanical strength of the polymer. The IR spectra of these materials vary according to their composition and is able to

show the occurrence of complexation and interaction between the various constituents. The vibrational spectra of chitosan film and chitosan added with 5 wt.% Al_2TiO_5 in the wavenumber region between 800 to 1700 and 2700 and 3600 cm^{-1} are shown in Fig. 6.1 (a) and (b). In the region between 800 to 1700 cm^{-1} , two characteristic peaks of chitosan can be observed at 1644 and 1559 cm^{-1} respectively. The band at 1559 cm^{-1} is attributed to the amine functional group and the band at 1644 cm^{-1} is assigned to carboxamide group of chitosan. The interaction between chitosan and filler is expected to occur via the amine, NH_2 and carboxamide, $\text{C}=\text{O}-\text{NHR}$ groups. The band assignments for chitosan as reported in the literature are listed in Table 6.1.

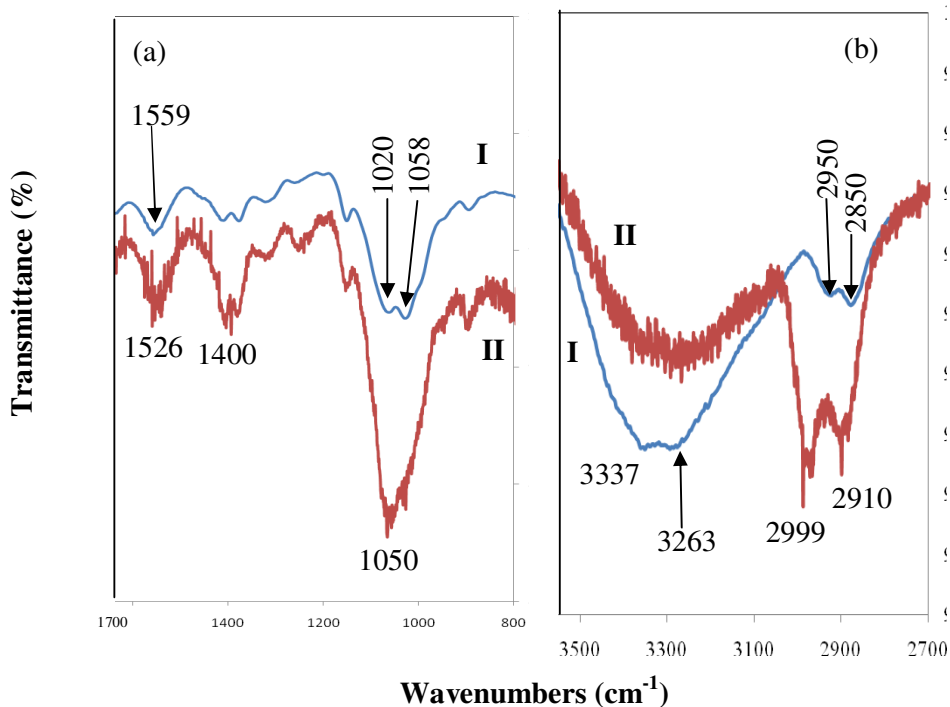


Fig. 6.1: The FTIR spectra of (I) chitosan and (II) chitosan added 5 wt.% Al_2TiO_5 in the region from (a) 800 to 1700 and (b) 2700 to 3600 cm^{-1} .

Table 6.1: Vibrational modes and wavenumbers exhibited by chitosan

Description of vibrations	Wavenumbers (cm ⁻¹)	References
carboxamide, C=O-NHR	1650 1636	Singh et. al,1997, Peniche et. al,1998, Muzarelli, 1977 and Aziz et. al, 2009.
Amine, NH ₂	1551 1590	Peniche et. al, 1998, Aziz et. al, 2009.
Ammonium, NH ₃ ⁺	~ 1514	Ritthidej et. al, 2002, Guan et. al, 1996,

It can be observed that the addition of different amounts of Al₂TiO₅ did not show any significant shift in the region between 800 to 1700 cm⁻¹. This implies that there is hardly any interaction between chitosan and the filler. In the region between 2700 to 3600 cm⁻¹ (Fig. 6.1(b)) bands at 2850 and 2950 cm⁻¹ shift to higher wavenumbers at 2910 and 2999 cm⁻¹ respectively. The small shift of one to two wavenumbers in the spectrum of chitosan and chitosan filler samples could possibly be due to hydrogen bonding between the chitosan and surface hydroxides on Al₂TiO₅.

6.3 The FTIR spectrum of chitosan – NH₄SCN

Fig. 6.2 shows IR spectra in the 1500-1700 cm⁻¹ region for the chitosan and chitosan-NH₄SCN salt complexes. When NH₄SCN was introduced into chitosan, the amine and carboxamide bands have shifted from 1559 and 1644 cm⁻¹ to lower wavenumbers at 1526 and 1629 cm⁻¹ respectively similar to CA-EC-LiCF₃SO₃. This has also been observed by Osman and Arof (2003). This is due to interactions between cation of the salt and the amine and carboxamide functional groups. The band at 2047 cm⁻¹ has been assigned to SCN⁻ [Aziz et. al, 2009], Fig. 6.3.

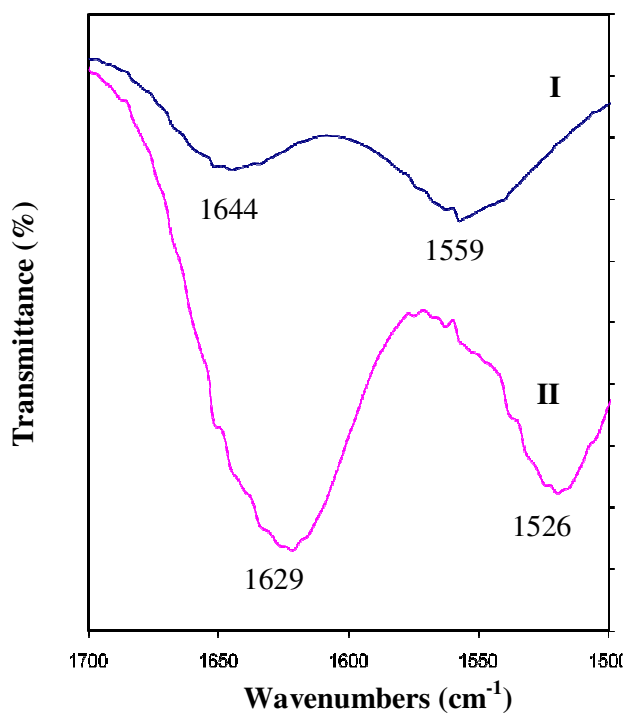


Fig. 6.2: The FTIR spectra of (I) chitosan and (II) chitosan – NH₄SCN in the region from 1500 to 1700 cm⁻¹

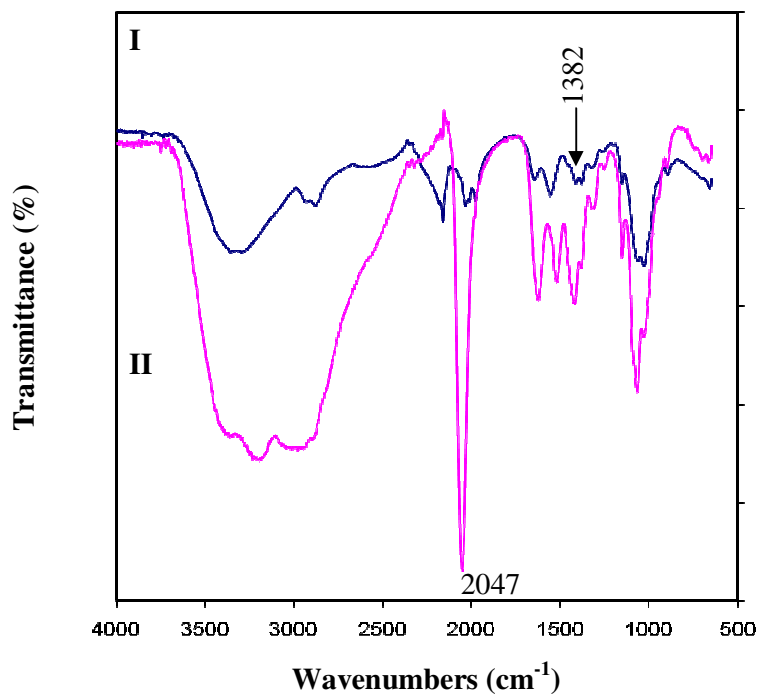


Fig. 6.3: The FTIR spectra of (I) chitosan and (II) chitosan – NH₄SCN in the region from 500 to 4000 cm⁻¹

According to Osman and Arof (2003), the ammonium, NH₃⁺ band appears as a small shoulder at ~1514 cm⁻¹ in the pure chitosan spectrum. In this work, the absence of

the NH_3^+ band in the pure CA spectrum is probably due to interaction between NH_3^+ of chitosan and the $-\text{COO}-$ of the acetic acid to form the $\text{O}=\text{C}-\text{NHR}$ band. This reaction is expected to happen when the CA film was stored in the dessicator for some time prior to infrared experiment [Ritthidej et. al, 2002].

The FTIR spectrum of CA films with NH_4SCN in the wavenumber region between 4000 to 1500 cm^{-1} is depicted in Fig. 6.4. Bands at 2047 cm^{-1} in the spectrum of chitosan- NH_4SCN is attributed to SCN^- vibration [Aziz et al., 2009]. The vibrational modes and wavenumbers exhibited by chitosan and chitosan - NH_4SCN are listed in Table 6.2. The incorporation of NH_4SCN to chitosan has also changed the region between 4000 and 2200 cm^{-1} and shifted the band at 1644 to 1629 cm^{-1} .

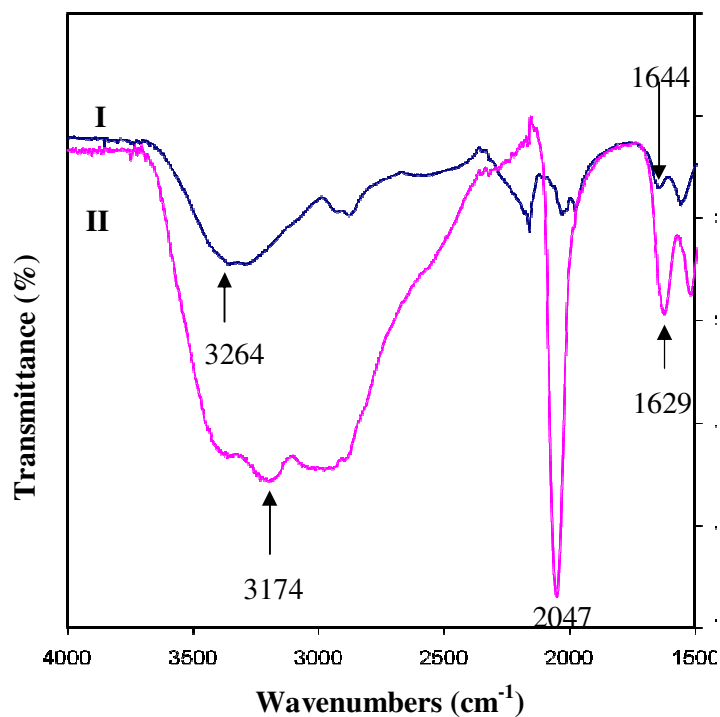


Fig. 6.4: The FTIR spectra of (I) chitosan and (II) chitosan – NH_4SCN in the region from 1500 to 4000 cm^{-1}

Table 6.2: The vibrational modes and wavenumbers exhibited by chitosan and chitosan-NH₄SCN.

Vibrational mode	Wavenumbers (cm ⁻¹)	
	Chitosan	Chitosan – NH ₄ SCN
CH ₂ bending	1420	1424
CH ₃ symmetrical deformation	1381	1383
Amine band, NH ₂	1559	1526
Carboxamide, C=O-NHR	1644	1629
Ambient anion, SCN-	-	2047

6.4 The FTIR spectrum of chitosan – NH₄SCN – Al₂TiO₅

This section will present the FTIR of chitosan-40 wt.% NH₄SCN the highest conducting polymer-salt complex doped with 5 wt.% of Al₂TiO₅. The amount of salt was fixed in the prepared sample. Fig. 6.5 shows the IR spectra in the 500-4000 cm⁻¹ region for the chitosan-salt and chitosan-salt-Al₂TiO₅ samples. The absorption bands at 1410 cm⁻¹ (CH₂ bending) and 1381 cm⁻¹ (CH₃ symmetrical deformation) shifted to higher wavenumbers of 1413 and 1385 cm⁻¹ after NH₄SCN and Al₂TiO₅ were added to chitosan as shown in Fig. 6.5. Similar observation has been reported in CA – NH₄SCN – Al₂O₃ electrolytes [Aziz et al., 2009].

Band at 2047 cm⁻¹ in the spectrum chitosan-NH₄SCN-Al₂TiO₅ is attributed to SCN⁻ vibration. With the addition of Al₂TiO₅ into the chitosan-NH₄SCN, it is observed that this band increase in intensity similar to that observed in the spectrum of PEO-NaSCN-AlCl₃ [Zhang et. al, 2006] and CA-NH₄SCN-Al₂O₃ electrolytes [Aziz et. al, 2009]. It is important to note that this band is not observed in the spectrum of chitosan acetate (Fig. 6.1). This observation indicates the interaction between chitosan –

NH_4SCN and chitosan- NH_4SCN - Al_2TiO_5 . From Fig. 6.7, band that peaks at 1629 cm^{-1} which is the carboxamide, $\text{C}=\text{O}-\text{NHR}$ group seem to increase in intensity as the amount of Al_2TiO_5 is increased. It is observed that this peak shifted from 1629 to 1634 cm^{-1} in the spectra of chitosan- NH_4SCN - Al_2TiO_5 complexes. Peak at 1618 cm^{-1} is correspond to OH vibration mode.

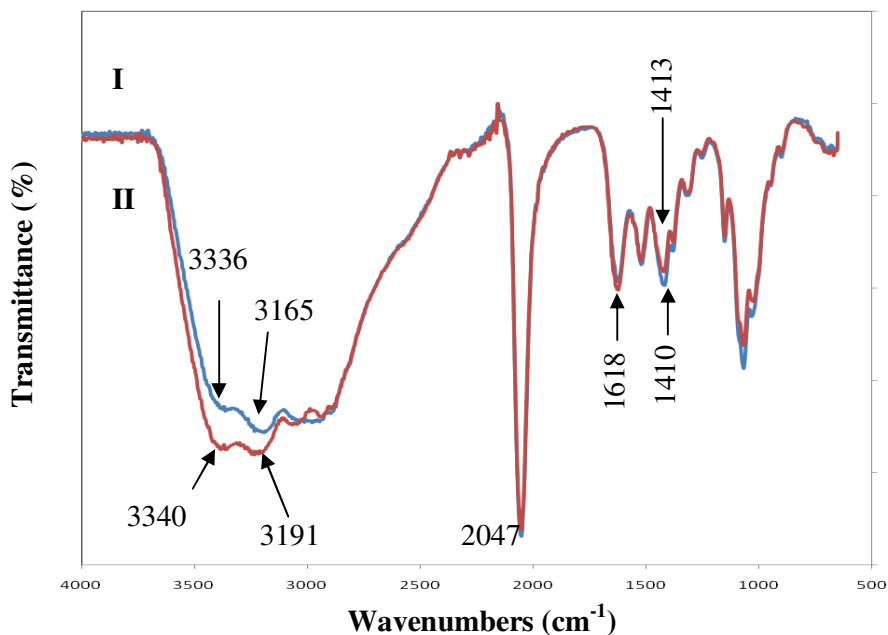


Fig. 6.5: The FTIR spectra of (I) chitosan- NH_4SCN and (II) chitosan- NH_4SCN - Al_2TiO_5 in the region from 500 to 4000 cm^{-1}

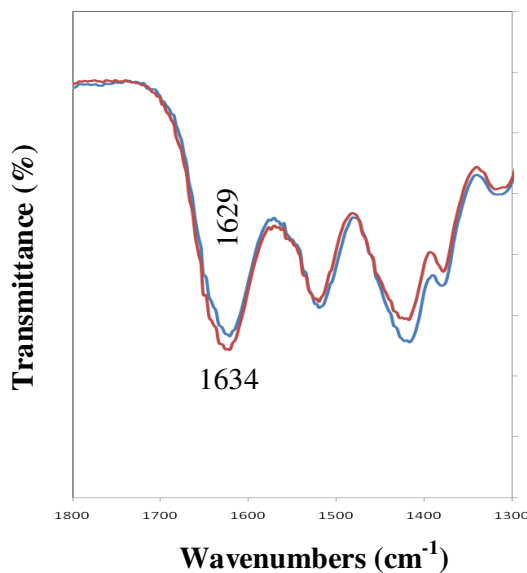


Fig. 6.6: The FTIR spectra of (I) chitosan- NH_4SCN and (II) chitosan- NH_4SCN - Al_2TiO_5 in the region from 1300 to 1800 cm^{-1}

6.5 Summary

From the FTIR spectrum studied, the chitosan film has amine and carboxamide bands at 1559 and 1644 cm^{-1} respectively. The ammonium thiocyanate salt interacted with chitosan since the amine and carboxamide bands in chitosan film have been noticed to shift from 1559, 1644 to 1526, 1629 cm^{-1} respectively. Interaction between the chitosan– Al_2TiO_5 system with the NH_4SCN salt is confirmed where carboxamide band have been observed to shift from 1629 to 1634 cm^{-1} wavenumbers. The presence of NH_4SCN is proven from the band at 2047 cm^{-1} . These result proved formation of chitosan- NH_4SCN complex and chitosan- NH_4SCN - Al_2TiO_5 complexes. From the result, the presence of hydroxide groups on Al_2TiO_5 can be implied. From this chapter it has been shown the chitosan- NH_4SCN complex and chitosan- NH_4SCN - Al_2TiO_5 composites have been found proving the achievement of the second objective of this dissertation.