CHAPTER 5

FTIR STUDIES

5.1 Introduction

This chapter presents the investigation on interactions between the electrolyte materials using FTIR analysis. The interaction can be revealed by the changes in the position and shape intensity of the bands’ peak. The interaction between the electrolyte materials prefers to take place in the amorphous region (Ramamohan & Sharma, 2013). According to Ratner and Shriver (as cited in Ulaganathan, Nithya, Rajendran, & Raghu, 2012), the ionic conduction in the polymer electrolyte occurs mainly in the amorphous region. Thus, the FTIR analysis can provide the evidence of the existence of ion in the complexation sites.

From the literature, the interaction between chitosan and salt occurred between the lone pair electron of oxygen or nitrogen atoms of chitosan and the conducting charge species (Majid & Arof, 2005, 2008; Morni et al., 1997; Yahya & Arof, 2003). Kadir, Aspanut, Majid and Arof (2011) reported that the cations of NH$_4$NO$_3$ are attached to the PVA-chitosan blend host due to the carboxamide, amine and hydroxyl bands experiencing a distinctive shift in the spectra. The shift in the hydroxyl band of pure starch film upon addition of salt proves the occurrence of starch-salt interaction (Khanmirzaei & Ramesh, 2013; Ramesh et al., 2011; Shukur, Ibrahim, Majid, Ithnin, & Kadir, 2013).
Apart from proving the interaction between the polymer host and the salt, FTIR analysis can also predict the conductivity trend (Kadir, Aspanut, Majid, & Arof, 2011; Mason, Hu, Glatzhofer, & Frech, 2010; Subban & Arof, 2004). The difference in the number of ions attached to the host functional groups should result in changes in the vibrational modes of the molecules in the polymer host. Besides, the effect of salt recrystallization on the conductivity can also be predicted. The schematic diagrams showing the interaction between the electrolyte components will be proposed.

5.2 FTIR Analysis of Starch Film

Figure 5.1 depicts the spectra of pure starch powder and pure starch film (S10C0) in the region that contains hydroxyl (OH) band.

![Figure 5.1: FTIR spectra for pure starch powder and S10C0 film in the region of 3000-3600 cm\(^{-1}\).](image-url)
The hydroxyl band in the spectrum of pure starch powder appears at 3290 cm\(^{-1}\) while that of S10C0 film appears at 3280 cm\(^{-1}\). Kadir, Aspanut, Majid, and Arof (2011) reported that the hydroxyl band in the spectrum of pure PVA powder has shifted from 3354 to 3343 cm\(^{-1}\) in the spectrum of pure PVA film. The authors claim that the band shift indicates the occurrence of interaction between polymer and the acetic acid solvent, which is relevant to our result. The strong and wide absorption in the hydroxyl band region of pure starch film indicates that there are several hydroxyl groups in starch (Teoh et al., 2012).

Figure 5.2(a) and (b) shows the spectra of pure starch powder and S10C0 film in the 1065-1095 cm\(^{-1}\) and 2850-2970 cm\(^{-1}\) regions, respectively.

![FTIR spectra for pure starch powder and S10C0 film in the region of (a) 1065-1095 cm\(^{-1}\) and (b) 2850-2970 cm\(^{-1}\).](image)

**Figure 5.2:** FTIR spectra for pure starch powder and S10C0 film in the region of (a) 1065-1095 cm\(^{-1}\) and (b) 2850-2970 cm\(^{-1}\).
starch (Ning, Xingxiang, Haihui, & Benqiao, 2009). As shown in the spectrum of S10C0 film, the intensity of this peak increases revealing the interaction between starch and acetic acid solvent in this band. Even though the wavenumber of this peak shows no significant shift, the changes in intensity and sharpness of the shape also provide the evidence of interaction between those materials (Ramesh & Liew, 2013). The same observation can be seen in the region of C-H stretching mode of starch in Figure 5.2(b). Although starch-acetic acid do not interact in this region, its FTIR spectra can also be affected, thus proves the starch-acetic acid interaction (Stygar, Zukowska, & Wieczorek, 2005).

Another evidence of starch-acetic acid interaction can be observed by the shifting of the peak in the region of 900-950 cm\(^{-1}\) as shown in Figure 5.3.

![Figure 5.3: FTIR spectra for pure starch powder and S10C0 film in the region of 900-950 cm\(^{-1}\).](image)
The peak observed in Figure 5.3 corresponds to the skeletal mode vibration of glycosidic linkage (C-O-C) (Juneja, Kaur, Odeku, & Singh, 2014; Khanmirzaei & Ramesh, 2013). This peak is located at 930 cm\(^{-1}\) in the spectrum of starch powder but shifts to 926 cm\(^{-1}\) in the spectrum of S10C0 film. This result indicates that the acetic acid has interacted with oxygen atoms in glycosidic linkages.

Figure 5.4 depicts the proposed schematic diagram of starch having an interaction with acetic acid.

![Schematic diagram of interaction between starch and acetic acid in S10C0 film. The dotted lines (---) represent dative bonds between cations and the complexation sites.](image)

Based on the FTIR results in Figures 5.1 to 5.3, the H\(^+\) ions from the acetic acid have interacted with the oxygen atoms in hydroxyl, C-O-C in the anhydroglucose ring and glycosidic linkages. This is because the oxygen atoms in those functional groups contain unused electrons which are known as lone pair electrons (Yap, 2012). The lone pair electrons can form a dative bond with the H\(^+\) ion as shown in Figure 5.4.
5.3 FTIR Analysis of Chitosan Film

Figure 5.5(a) depicts the spectra of pure chitosan powder and pure chitosan film (S0C10) in the region of hydroxyl band. There is a change in intensity of the peak at 3354 cm\(^{-1}\) revealing the interaction between chitosan and acetic acid solvent in the hydroxyl band. The position of the hydroxyl band for S0C10 film is in good agreement with that reported by Kadir, Asnanut, Majid, and Arof (2011).

![Figure 5.5(a) FTIR spectra for pure chitosan powder and S0C10 film in the region of 3000-3600 cm\(^{-1}\).](image)

**Figure 5.5**: FTIR spectra for pure chitosan powder and S0C10 film in the region of (a) 3000-3600 cm\(^{-1}\) and (b) 1540-1560 cm\(^{-1}\).

Figure 5.5(b) depicts the spectra of pure chitosan powder and S0C10 film in the region that contains amine (NH\(_2\)) band. The amine band is observed at 1547 cm\(^{-1}\) in the spectrum of pure chitosan powder. In the spectrum of S0C10 film, this band is located at 1549 cm\(^{-1}\) proving the interaction between the acetic acid solvent and the nitrogen
donor of chitosan. Buraidah (2012) and Osman and Arof (2003) also inferred the occurrence of chitosan-acetic acid interaction at the nitrogen atom of amine based on the shifting of amine band’s position.

During the deacetylation process of chitin, carboxamide (O=C-NHR) band is removed to release amine band (Badawy & Rabea, 2011; Zakaria, Izzah, Jawaid, & Hassan, 2012). However, due to incomplete deacytelaion process, the presence of carboxamide band in chitosan is still there (Buraidah, 2012). Figure 5.6 shows FTIR spectra of pure chitosan powder and S0C10 film in the region that contains the carboxamide band. The carboxamide band in the spectra of pure chitosan powder and S0C10 film is located at 1652 cm\(^{-1}\). However, change in intensity of the peak can be observed thus provides the evidence of the interaction between acetic acid solvent and chitosan in carboxamide band.

Figure 5.6: FTIR spectra for pure chitosan powder and S0C10 film in the region of 1585-1665 cm\(^{-1}\).
In Figure 5.7(a), two peaks appear at 1074 and 1022 cm\(^{-1}\) in the spectrum of chitosan powder. These peaks are assigned to C-O-C stretching vibration (Nivethaa, Narayanan, & Stephen, 2014). In the spectrum of S0C10 film, these two peaks shift to 1062 and 1025 cm\(^{-1}\) accompanied by the increase in intensity indicating the involvement of this band in chitosan-acetic acid interaction. In Figure 5.7(b), a peak corresponding to glycosidic bonding (C-O-C) vibration appears at 897 cm\(^{-1}\) in the spectrum of chitosan powder but shift to 895 cm\(^{-1}\) with an increase in intensity in the spectrum of S0C10 film.

![Figure 5.7](image)

**Figure 5.7:** FTIR spectra for pure chitosan powder and S0C10 film in the region of (a) 1000-1100 cm\(^{-1}\) and (b) 850-920 cm\(^{-1}\).

Based on the results in Figures 5.5 to 5.7, the schematic diagram of proposed interaction between chitosan and acetic acid solvent is shown in Figure 5.8.
5.4 FTIR Analysis of Starch-Chitosan

In a polymer blend, the interaction between the two polymer components occurs through hydrogen bonding (Bouslah & Amrani, 2007; Luo, Hu, Zhao, Goh, & Li, 2003). From a report by Luo et al. (2003), the hydrogen bonding interaction in the blend of poly(4-methyl-5-vinylthiazole) (PMVT) and poly(p-vinylphenol) (PVPh) is proven by the shifting of hydroxyl band of pure PVPh upon addition of PMVT.

Figure 5.9 shows the spectra of S0C10, S10C0 and starch-chitosan blend with the ratio of 80:20 (S8C2) in the hydroxyl band and amine band regions. In Figure 5.9(a), the hydroxyl band in the spectrum of S0C10 film appears at 3354 cm\(^{-1}\). In the spectrum of S10C0 film, hydroxyl band appears at 3280 cm\(^{-1}\). The mixture of two or more materials will reflect the physical blends and chemical reactions based on the changes in characteristics spectral peaks (Ashori & Bahrami, 2014). In the spectrum of S8C2 film,
the hydroxyl band has shifted to 3288 cm\(^{-1}\). In Figure 5.9(b), the amine band of S0C10 film is located at 1549 cm\(^{-1}\). In the spectrum of S8C2 film, the amine band has shifted to 1548 cm\(^{-1}\). Bajer and Kaczmarek (2010) reported that the position of the amine band of chitosan shifted from 1561 to 1560 cm\(^{-1}\) in starch-chitosan film. Based on Figure 5.9, starch-chitosan interaction may occur between hydroxyl groups of starch and the hydroxyl groups of chitosan as well as between hydroxyl groups of starch and the amine groups of chitosan.

![Figure 5.9: FTIR spectra for S0C10, S10C0 and S8C2 films in the region of (a) 3000-3500 cm\(^{-1}\) and (b) 1540-1560 cm\(^{-1}\).](image)

Figure 5.10 depicts the FTIR spectra of S0C10 and S8C2 films in the carboxamide band region. No peak shifting is observed. Besides, no significant change in intensity can be seen inferring that no interaction occurs between chitosan and starch at the carboxamide band.
Figure 5.10: FTIR spectra for S0C10 and S8C2 films in the region of 1585-1665 cm\(^{-1}\).

Figure 5.11 represents the spectra of S0C10, S10C0 and S8C2 films in the 1010-1100 cm\(^{-1}\) and 880-950 cm\(^{-1}\) regions.

Figure 5.11: FTIR spectra for S0C10, S10C0 and S8C2 films in the region of (a) 1010-1100 cm\(^{-1}\) and (b) 880-950 cm\(^{-1}\).
From Figure 5.11(a), the C-O bond stretching peak at 1077 cm\(^{-1}\) in the spectrum of S10C0 film is observed unshifted in the spectrum of S8C2 film. Besides, no significant change in intensity can be seen indicating that the oxygen atom in anhydroglucose ring of starch does not involve in hydrogen bonding interaction with chitosan. In Figure 5.11(b), the peak corresponds to glycosidic linkage of starch at 926 cm\(^{-1}\) has shifted to 929 cm\(^{-1}\) upon blending starch with chitosan, inferring the interaction occurs in this region. It is noticed that the C-O-C stretching vibration peaks and glycosidic bonding (C-O-C) vibration peak in the spectrum of S0C10 film do not appear in the spectrum of S8C2 film. The absence of those peaks suggests good miscibility between starch and chitosan in the blend, mainly due to the hydrogen bond interaction between hydroxyl groups of starch with amino and hydroxyl groups of chitosan (El-Hefian, Nasef, & Yahaya, 2010; El-Hefian, Nasef, Yahaya, & Khan, 2010; Ramya, Sudha, & Mahalakshmi, 2012; Thenmozhi, Gomathi, & Sudha, 2013). According to Viswanathan and Dadmun (2002), the formation of hydrogen bonds between two polymers in a blend enhances the miscibility between the polymers. Thus, the FTIR result further strengthens the DSC and SEM analysis on starch-chitosan miscibility as presented in Chapter 4.

In starch-chitosan blend, the interaction occurs mainly through hydrogen bonding between the amylose of starch and chitosan molecules as it is easier for amylose to mix with chitosan than the branched chain amylopectin (Mathew & Abraham, 2008). This is because the branching structure in amylopectin has greater steric hindrance and thus prevents chemical reactions rather than the linear structure of the amylose (Khiai & Arof, 2010). The schematic diagram of proposed interaction between starch, chitosan and acetic acid in S8C2 film is depicted in Figure 5.12.
Figure 5.12: Schematic diagram of interaction between starch, chitosan and acetic acid in S8C2 film. The black dotted lines (-----) represent dative bonds between cations and the complexation sites. The green lines (-----) represent hydrogen bonds between starch and chitosan.
5.5 FTIR Analysis of Starch-Chitosan-NH$_4$Cl

Figure 5.13 shows the FTIR spectra for selected electrolytes in starch-chitosan-NH$_4$Cl (salted) system in the region of hydroxyl band. The hydroxyl band is located at 3288 cm$^{-1}$ in the spectrum of S8C2 film. However, the hydroxyl band has shifted to lower wavenumbers of 3284, 3278 and 3264 cm$^{-1}$ on addition of 5, 10 and 25 wt.% NH$_4$Cl (S1, S2 and S5 electrolytes, respectively). Kadir, Aspan, Yahya, and Arof

![Figure 5.13: FTIR spectra for S8C2, pure NH$_4$Cl salt and selected electrolytes in the salted system in the region of 2950-3650 cm$^{-1}$.](image-url)
(2011) reported that the interaction between chitosan and NH$_4$NO$_3$ at hydroxyl band is evidenced by the shifting of the hydroxyl band to lower wavenumbers. Thus it can be concluded that the polymer host in the present work has interacted with NH$_4$Cl at the hydroxyl band. In the spectrum of S8 electrolyte, two peaks appear at 3112 and 3016 cm$^{-1}$, corresponding to the asymmetry vibration ($v_{as}$(NH$_4^+$)) and symmetry vibration ($v_s$(NH$_4^+$)) modes of NH$_4^+$, respectively. Those two peaks are located at 3111 and 3010 cm$^{-1}$, respectively, in the spectrum of pure NH$_4$Cl salt. The appearance of $v_{as}$(NH$_4^+$) and $v_s$(NH$_4^+$) modes infers the occurrence of ion reassociation when more than 25 wt.% NH$_4$Cl is added to the electrolyte. The reassociation of ions has formed ion aggregates. According to Mason et al. (2010), the higher aggregation had resulted in fewer available charge carriers in their polymer electrolyte system resulting in conductivity decrement. In the present work, it can be inferred that the addition of more than 25 wt.% NH$_4$Cl would decrease the conductivity of electrolyte due the formation of ion aggregates.

Figure 5.14 represents the FTIR spectra for selected electrolytes in salted system in the carboxamide band region. In the spectrum of S8C2 film, the carboxamide band is located at 1652 cm$^{-1}$. As the NH$_4$Cl content increases to 25 wt.%, the carboxamide band shifts to lower wavenumbers. The carboxamide band appears at 1629 cm$^{-1}$ in the spectrum of S5 electrolyte. This result again provides the evidence of starch-chitosan-NH$_4$Cl interaction. In the spectrum of S6 and S7 electrolytes, the carboxamide band shift back to higher wavenumbers of 1632 and 1633 cm$^{-1}$, respectively. This phenomenon may be attributed to the decrease in number density of ions resulting in the reduction of interaction between the salt and the polymer host at the oxygen atoms of carboxamide band.
The amine band is located at 1548 cm\(^{-1}\) in the spectrum of S8C2 film as shown in Figure 5.15. In the spectrum of S1 electrolyte, the amine band is observed at 1532 cm\(^{-1}\) and further shifted to 1526 and 1524 cm\(^{-1}\) in the spectra of S5 and S6 electrolytes.

This result provides the evidence of starch-chitosan-NH\(_4\)Cl interaction at the nitrogen atom of amine group. In the spectrum of S8 electrolyte, the amine band’s peak does not appear suggesting that the ions had reassociated back to form neutral ion pairs, which can lead to the conductivity decrement.

Figure 5.14: FTIR spectra for S8C2 and selected electrolytes in the salted system in the region of 1585-1665 cm\(^{-1}\).
In the spectrum of S2, S3 and S5 electrolytes in Figure 5.16, the peak which corresponds to C-O-C group has shifted to lower wavenumbers of 1076, 1075 and 1074 cm$^{-1}$, respectively. This result indicates that the cations have interacted with oxygen atoms in C-O-C group and further prove the interaction of polymer host with NH$_4$Cl. In the spectrum of S6 electrolyte, the C-O bond stretching band has shifted to higher

![Figure 5.15: FTIR spectra for S8C2, pure NH$_4$Cl salt and selected electrolytes in the salted system in the region of 1480-1570 cm$^{-1}$.](image)
wavenumber of 1075 cm\(^{-1}\). No peak is observed in the spectrum of S8 electrolyte indicating the recrystallization of the salt which can lead to the decrease in conductivity.

**Figure 5.16**: FTIR spectra for S8C2, pure NH\(_4\)Cl salt and selected electrolytes in the salted system in the region of 1065-1095 cm\(^{-1}\).

From Figure 5.17, the peak which corresponds to glycosidic linkage at 929 cm\(^{-1}\) in the spectrum of S8C2 film is observed to shift to 934 cm\(^{-1}\) in the spectrum of S2, S3, S5 and S6 electrolytes. The present result proves that the cations from NH\(_4\)Cl interact
with oxygen atoms in the glycosidic linkages of polymer host. No peak is observed in the spectrum of S8 electrolyte indicating the recrystallization of the salt which can lead to the decrease in conductivity.

![FTIR spectra for S8C2 film, pure NH₄Cl salt and selected electrolytes in the salted system in the region of 900-950 cm⁻¹.](image)

**Figure 5.17:** FTIR spectra for S8C2 film, pure NH₄Cl salt and selected electrolytes in the salted system in the region of 900-950 cm⁻¹.

The proposed interaction between starch-chitosan blend with NH₄Cl and acetic acid solvent is illustrated in Figure 5.18.
Figure 5.18: Schematic diagram of interaction between starch, chitosan, NH$_4$Cl and acetic acid. The black dotted lines (----) represent dative bonds between cations and the complexation sites. The green lines (H|H|H|H) represent hydrogen bonds between starch and chitosan.
5.6 FTIR Analysis of Starch-Chitosan-Glycerol

Figure 5.19(a) depicts the FTIR spectra in the hydroxyl band region for S8C2, pure glycerol and starch-chitosan-glycerol films. The peak which is located at 3288 cm\(^{-1}\) in the spectrum of S8C2 film has shifted to 3291 cm\(^{-1}\) after the addition of 5 wt.% glycerol. The peak has further shifted to 3294 cm\(^{-1}\) on addition of 35 wt.% glycerol. Glycerol has multi-hydroxyl moiety structure and possesses the strong ability to interact with the polysaccharide matrix through hydrogen bonding interactions (Liang, Huang, Liu, & Yam, 2009). Based on Figure 5.19(a), it can be indicated that glycerol and the

![Figure 5.19](image-url)

**Figure 5.19**: FTIR spectra for S8C2 film, pure glycerol and starch-chitosan-glycerol films in the region of (a) 3000-3600 cm\(^{-1}\) and (b) 1585-1665 cm\(^{-1}\).
polymer blend have formed hydrogen bonding at the hydroxyl groups of both materials. The interaction between starch-chitosan blend and glycerol is further evidenced by the shifting of carboxamide band towards lower wavenumbers as the glycerol concentration increases to 15 wt.% as shown in Figure 5.19(b). When 35 wt.% glycerol is added to the polymer, the carboxamide band has shifted back to higher wavenumber of $1646 \text{ cm}^{-1}$. At 35 wt.% concentration, the interaction between polymer and glycerol may be decreased since there is competition between the plasticizer molecules to form hydrogen bonding with the polymer molecules. Thus, this phenomenon may leads to the increase in glycerol-glycerol interaction instead of polymer-glycerol interaction. Figure 5.20 shows the FTIR spectra of starch-chitosan-glycerol films in the amine band region.

![FTIR spectra for starch-chitosan-glycerol films in the region of 1500-1600 cm$^{-1}$](image)

**Figure 5.20**: FTIR spectra for starch-chitosan-glycerol films in the region of 1500-1600 cm$^{-1}$. 
From Figure 5.20, the amine band peak is observed to locate at 1554, 1569 and 1567 cm\(^{-1}\) with the addition of 5, 25 and 35 wt.% glycerol indicating the interaction between polymer and glycerol in this band.

![FTIR spectra for S8C2 and starch-chitosan-glycerol films in the region of 1065-1095 cm\(^{-1}\).](image)

**Figure 5.21:** FTIR spectra for S8C2 and starch-chitosan-glycerol films in the region of 1065-1095 cm\(^{-1}\).

From Figure 5.21, the peak which corresponds to C-O bond stretching of C-O-C group at 1077 cm\(^{-1}\) in the spectrum of S8C2 film is observed to shift to 1079 cm\(^{-1}\) as the glycerol content increases to 25 wt.%. Thus, it can be inferred that the hydroxyl groups of glycerol have interacted with oxygen atoms in the C-O-C group.
From Figure 5.22, the peak at 929 cm\(^{-1}\) in the spectrum of S8C2 film has shifted to 932, 933, 927 and 925 cm\(^{-1}\) on addition of 5, 15, 25 and 35 wt.% glycerol, respectively. These results indicate the occurrence of interaction between the polymer blend and glycerol at glycosidic linkages.

From Figure 5.22, the peak at 929 cm\(^{-1}\) in the spectrum of S8C2 film has shifted to 932, 933, 927 and 925 cm\(^{-1}\) on addition of 5, 15, 25 and 35 wt.% glycerol, respectively. These results indicate the occurrence of interaction between the polymer blend and glycerol at glycosidic linkages.

The proposed interaction between starch-chitosan blend with glycerol and acetic acid solvent is illustrated in Figure 5.23.

**Figure 5.22:** FTIR spectra for S8C2 and starch-chitosan-glycerol films in the region of 900-950 cm\(^{-1}\).
Figure 5.23: Schematic diagram of interaction between starch, chitosan, acetic acid and glycerol. The black dotted lines (-----) represent dative bonds between cations and the complexation sites. The green lines (--------) represent hydrogen bonds between starch, chitosan and glycerol.
5.7 FTIR Analysis of Glycerol-NH$_4$Cl

For a plasticized electrolyte, it is important to determine if there is interaction between the salt and the plasticizer. If the interaction occurs, then interaction should occur between the cation of the salt and the hydroxyl group of glycerol. Figure 5.24 shows the FTIR spectra of pure glycerol and glycerol mixed with different weight percentage of NH$_4$Cl.

![Figure 5.24: FTIR spectra for pure glycerol and glycerol with 1, 4 and 7 wt.% NH$_4$Cl in the region of 3000-3600 cm$^{-1}$.](image)

The peak of hydroxyl band has shifted from 3286 cm$^{-1}$ to the lower wavenumbers of 3281, 3279 and 3276 cm$^{-1}$ on addition of 1, 4 and 7 wt.% NH$_4$Cl,
respectively. The peak shifting proves the interaction between the \( \text{NH}_4^+ \) ion and the oxygen atom of glycerol molecule. The schematic diagram in Figure 5.25 presents the possible interaction between glycerol and \( \text{NH}_4\text{Cl} \).

![Schematic diagram of interaction between glycerol and \( \text{NH}_4\text{Cl} \). The black dotted line (-----) represents dative bond between cation and the complexation site.](image)

**Figure 5.25:** Schematic diagram of interaction between glycerol and \( \text{NH}_4\text{Cl} \). The black dotted line (-----) represents dative bond between cation and the complexation site.

### 5.8 FTIR Analysis of Starch-Chitosan-\( \text{NH}_4\text{Cl} \)-Glycerol

FTIR spectra for the selected electrolytes in plasticized system in the hydroxyl band region are shown in Figure 5.26. The hydroxyl band has shifted to lower wavenumber of 3254 cm\(^{-1}\) on addition of 30 wt.% glycerol (P6 electrolyte) and further shifted to 3247 cm\(^{-1}\) on addition of 35 wt.% glycerol (P7 electrolyte). Apart from hydrogen bonding formation with the polymer host, the addition of plasticizer also promote ion dissociation, thus more ions have interacted with the polymer host at the hydroxyl band as evidenced by the shifting of FTIR spectra in Figure 5.26. This phenomenon can assist the conductivity enhancement. In the spectrum of P8 electrolyte,
the hydroxyl band has shifted to higher wavenumber of 3301 cm\(^{-1}\). Less ions interact with the polymer host at the hydroxyl band, resulting in a shift to higher wavenumber of FTIR spectrum in Figure 5.26.

![Figure 5.26: FTIR spectra for S5 and selected electrolytes in plasticized system in the region of 2950-3650 cm\(^{-1}\).](image)

Figure 5.27 represents the FTIR spectra for selected electrolytes in plasticized system in the carboxamide band region. In the spectrum of S5 film, the carboxamide band is located at 1629 cm\(^{-1}\). As the glycerol content increases to 35 wt.\%, the carboxamide band has shifted to higher wavenumbers. The carboxamide band appears
at 1638 cm\(^{-1}\) in the spectrum of P7 electrolyte. In the spectrum of P8 electrolyte, the carboxamide band has shifted back to lower wavenumber of 1636 cm\(^{-1}\).

FTIR spectra for the selected electrolytes in plasticized system in the amine band region are shown in Figure 5.28. The amine band is located at 1526 cm\(^{-1}\) in the spectrum of S5 electrolyte. The amine band has shifted to lower wavenumbers of 1525, 1524 and 1585 cm\(^{-1}\).
1523 cm\(^{-1}\) in the spectra of P2, P3 and P5 electrolytes. With the addition of plasticizer, more ions interact with the nitrogen donor of chitosan in starch-chitosan blend host.

![FTIR spectra](image)

**Figure 5.28:** FTIR spectra for S5 and selected electrolytes in plasticized system in the region of 1500-1590 cm\(^{-1}\).

In the spectrum of P1 electrolyte in Figure 5.29(a), the peak corresponding to C-O bond stretching of C-O-C group has shifted from 1074 cm\(^{-1}\) to 1073 cm\(^{-1}\). As the glycerol content in the electrolyte increases to 10 and 15 wt.%., the peak shifts to lower wavenumbers of 1072 cm\(^{-1}\) and 1071 cm\(^{-1}\), respectively. This result indicates that more ions have interacted with oxygen atoms in C-O-C group as glycerol content increases.
From Figure 5.29(b), the peak corresponding to glycosidic linkage at 934 cm\(^{-1}\) in the spectrum of S5 electrolyte is observed to shift to higher wavenumber as glycerol content increases. The present result proves that more NH\(_4^+\) cations from NH\(_4\)Cl interact with oxygen atoms in the glycosidic linkages with the addition of glycerol. The proposed interaction between starch-chitosan blend with NH\(_4\)Cl, acetic acid solvent and glycerol is illustrated in Figure 5.30.

**Figure 5.29:** FTIR spectra for S5 and selected electrolytes in plasticized system in the region of (a) 1065-1095 cm\(^{-1}\) and (b) 900-950 cm\(^{-1}\).
Figure 5.30: Schematic diagram of interaction between starch, chitosan, acetic acid, NH\textsubscript{4}Cl and glycerol.
5.9 Summary

From FTIR analysis on starch and chitosan films, starch-acetic acid and chitosan-acetic acid interactions occur at the oxygen atoms of hydroxyl, C-O-C and glycosidic linkages of the polymers. Chitosan-acetic acid interaction also occurs at the carboxamide and amine bands. Upon blending 80 wt.% starch with 20 wt.% chitosan, the shift of the peak at hydroxyl and amine bands as well as the glycosidic linkage of starch proves the involvement of these functional groups in hydrogen bonding formation. When NH₄Cl was added to the starch-chitosan blend, cations are inferred to interact with oxygen atoms of hydroxyl, carboxamide, C-O-C and glycosidic linkage. Nitrogen atom of amine band is also inferred to provide the coordination site for the cations by the shifting of the band to lower wavenumbers on addition of salt. The interaction between glycerol and NH₄Cl is proven by the shifting of the hydroxyl band’s peak of glycerol to lower wavenumbers on addition of salt. The shift in peak’s position of hydroxyl, carboxamide, amine, C-O-C and glycosidic linkage spectra proves the starch-chitosan-glycerol interaction. From the FTIR analysis on starch-chitosan-NH₄Cl-glycerol, the addition of glycerol has dissociated more salt hence more ions interact with the polymer host. It is also inferred that glycerol is able to provide additional pathways for the ions to conduct.