FTIR studies of plasticized poly(vinyl alcohol)–chitosan blend doped with NH₄NO₃ polymer electrolyte membrane

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Fourier transform infrared (FTIR) spectroscopy studies of poly(vinyl alcohol) (PVA), and chitosan polymer blend doped with ammonium nitrate (NH₄NO₃) salt and plasticized with ethylene carbonate (EC) have been performed with emphasis on the shift of the carboxamide, amine and hydroxyl bands. 1% acetic acid solution was used as the solvent. It is observed from the chitosan film spectrum that evidence of polymer–solvent interaction can be observed from the shifting of the carboxamide band at 1660 cm⁻¹ and the amine band at 1591 cm⁻¹ to 1650 and 1557 cm⁻¹ respectively and the shift of the hydroxyl band from 3377 to 3354 cm⁻¹. The hydroxyl band in the spectrum of PVA powder is observed at 3354 cm⁻¹ and is observed at 3343 cm⁻¹ in the spectrum of the PVA film. On addition of NH₄NO₃ up to 30 wt.%, the carboxamide, amine and hydroxyl bands shifted from 1650, 1557 and 3354 cm⁻¹ to 1642, 1541 and 3348 cm⁻¹ indicating that the chitosan has complexed with the salt. In the PVA–NH₄NO₃ spectrum, the hydroxyl band has shifted from 3343 to 3272 cm⁻¹ on addition of salt from 10 to 30 wt.%. EC acts as a plasticizing agent since there is no shift in the bands as observed in the spectrum of PVA–chitosan–EC films. The mechanism of ion migration is proposed for the plasticized and unplasticized PVA–chitosan–NH₄NO₃ systems. In the spectrum of PVA–chitosan–NH₄NO₃–EC complex, the doublet C=O stretching in EC is observed in the vicinity 1800 and 1700. This indicates that there is some interaction between the salt and EC.

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1. Introduction

Polymer blends has attracted the attention of many researchers. This is due to the possibility of developing new materials from polymer blends. The properties of the blend are different and better than the properties of the single polymer [1–3]. For example, the conductivity of a polymer electrolyte can be improved if the host is a blend of two polymers [4–6]. Polymer blending can guarantee structural stability [7]. Poly(methylmethacrylate) (PMMA) and poly(vinylidene fluoride) (PVdF) [8], PMMA and poly(vinyl alcohol) (PVA) [4], poly(vinyl chloride) (PVC) and PVdF [9], chitosan and poly(ethylene oxide) (PEO) [10] are among polymeric blends that have been previously studied. Chitosan is a natural polymer and its chemical structure (1→4)-2-amino-2-deoxy-β-d-glucan, contains N-deacetylated derivatives of chitin, (1→4)-2-acetamido-2-deoxy-β-d-glucan [11–13]. Chitosan has been used in many applications for example as separators in medicine and biotechnology [14], for the removal of heavy metals and radioisotopes to prevent water pollution [15] as food packaging materials [16] and dietary fiber and a potential medicine against hypertension [17]. In our laboratory, polymer electrolyte based on chitosan has been studied [18–22] for potential application in electrochemical devices such as batteries [23–25]. Donoso et al. [26] have shown that the nitrogen atoms in chitosan serve as complexation sites for cation coordination. Chitosan is biocompatible and biodegradable [27]. Chitosan also blends with other polymer [3] and is expected to be used in the development of composite materials since it has many functional groups [28–29]. Chitosan blend based polymer electrolytes [30–32] have been used in electrochemical devices such as solar cells [33–34] and super capacitors [35]. In a previous work, we have prepared polymer electrolyte based on PVA–chitosan blends and applied the electrolyte in a primary and a secondary battery [36]. In the biomedical field it has been reported that the membrane formed from chitosan and PVA blend is more favorable for cell culture compared to pure PVA membrane [37]. PVA is a semi crystalline polymer with carbon chain backbone and hydroxyl groups attached to the methane carbons [4]. PVA is a highly hydrophilic, non toxic and low cost polymer with good mechanical strength, thermal stability, chemical stability and excellent film forming properties [38]. PVA is biocompatible, non toxic and exhibits minimal cell adhesion and protein absorption. PVA membrane has formed application in the biomedical field [39]. Polymer electrolyte based on PVA has been reported to exhibit good conductivity [40–42] and the polymer
electrolyte based on PVA is potentially employed in the application of electrochemical devices such as lithium [43] and zinc air batteries [44], fuel cells [45] and electric double layer capacitors [46]. Hema et al. [47] have shown that in PVA based polymers, the conduction takes place when protons from the salt hops via each coordinating site (oxygen) of the polymer host. From our previous work [36], conductivity of the polymer–NH₄NO₃ electrolyte with 40 wt.% NH₄NO₃ was $2.07 \times 10^{-5}$ Sc m⁻¹ and when plasticized with 70 wt.% EC, the conductivity increased to $1.60 \times 10^{-3}$ Sc m⁻¹. X-ray diffraction and scanning electron microscopy studies have shown that concentration of NH₄NO₃ salt influences the conductivity since the diffractogram of the sample with crystalline structures protruding its surface shows peaks that can be attributed to the salt. With more salt crystallizing out of the sample surface the number of mobile ions that can contribute to conductivity decreases. To further discuss the phenomena such as salt–polymer complexation, ion aggregation formation and interaction between the salt and plasticizer in the sample, FTIR was employed. This paper reports some details of interactions between polymer–polymer, polymer–salt, polymer–plasticizer, polymer–salt–plasticizer and salt–plasticizer with emphasis at the carboxamide, amine and hydroxyl groups present in the polymers.

2. Experimental

2.1. Sample preparation

To study the FTIR in the present work, 7 systems were prepared

Chitosan–PVA,
Chitosan–NH₄NO₃,
PVA–NH₄NO₃.

![Fig. 1](image)

(a) FTIR spectra of (i) pure chitosan powder, (ii) pure chitosan film and (iii) PVA–chitosan blend with the ratio of 3:2 in the region of carboxamide and amine bands. (b) FTIR spectra of (i) pure PVA, (ii) PVA film, (iii) pure chitosan powder, (iv) pure chitosan film and (v) PVA–chitosan blend with the ratio of 3:2 in the region of hydroxyl band.

![Fig. 2](image)

(a) FTIR spectra of (i) pure chitosan film and pure chitosan film with (ii) 10 wt.% NH₄NO₃, (iii) 30 wt.% NH₄NO₃, (iv) 50 wt.% NH₄NO₃ and (v) pure NH₄NO₃ salt in the 3000–3700 cm⁻¹ spectra region. (b) FTIR spectra of (i) pure chitosan film and pure chitosan film with (ii) 20 wt.% NH₄NO₃, (iii) 30 wt.% NH₄NO₃, (iv) 40 wt.% NH₄NO₃ and (v) 50 wt.% NH₄NO₃ in the 1490–1700 cm⁻¹ spectra region. (c) FTIR spectra of (i) pure chitosan film and pure chitosan film with (ii) 20 wt.% NH₄NO₃, (iii) 30 wt.% NH₄NO₃, (iv) 40 wt.% NH₄NO₃, (v) 50 wt.% NH₄NO₃ and (vi) pure NH₄NO₃ salt in the symmetric (NO₃⁻) vibration mode spectra region.
Fig. 3. (a) FTIR spectra of (i) pure PVA film and PVA with (ii) 10 wt.% NH₄NO₃, (iii) 20 wt.% NH₄NO₃, (iv) 30 wt.% NH₄NO₃, (v) 50 wt.% NH₄NO₃ and (vi) pure NH₄NO₃ salt in the 3000–3700 cm⁻¹ spectra region. (b) FTIR spectra of (i) pure PVA film and PVA with (ii) 10 wt.% NH₄NO₃, (iii) 40 wt.% NH₄NO₃ and (iv) pure NH₄NO₃ salt in the symmetric (NO₃⁻) vibration mode spectra region.

PVA–chitosan–EC,
PVA–chitosan–NH₄NO₃,
PVA–chitosan–NH₄NO₃–EC,
EC–NH₄NO₃.

PVA with molecular weight 10,000 g mol⁻¹, highly viscous chitosan powder and EC were procured from Aldrich Chemical Co. Glacial acetic acid was procured from AJAX Chemicals. 1% acetic acid solution was used as the solvent and all films were prepared using the solution cast technique.

2.2. Sample characterization

2.2.1. Fourier transform infrared (FTIR) spectroscopy

Thermo Scientific/Nicolet iS10 FTIR spectrometer was used to record the FTIR spectra with 1 cm⁻¹ resolution in the transmission mode from wave numbers 650–4000 cm⁻¹. Confirmation of complexation and proposition of the conduction mechanism of

Fig. 4. (a) FTIR spectra of pure PVA–chitosan blend and PVA–chitosan blend with 50 wt.% EC in the 2990–3590 cm⁻¹ spectra region. (b) FTIR spectra of pure PVA–chitosan blend film with 30 wt.% EC and 50 wt.% EC in the 1505–1685 cm⁻¹ spectra region.

Fig. 5. (a) FTIR spectra of (i) pure EC, (ii) EC mixed with 0.5 wt.% of NH₄NO₃ and (iii) EC mixed with 1.1 wt.% of NH₄NO₃ in the region C=O bending band. (b) FTIR spectra of (i) pure EC, (ii) EC mixed with 0.5 wt.% of NH₄NO₃ and (iii) EC mixed with 1.1 wt.% of NH₄NO₃ in the region of C–O stretching band.
the charge carriers were the objectives of performing FTIR spectroscopy.

3. Results and discussion

3.1. FTIR spectra of PVA–chitosan blend

The carboxamide O–C–NHR band in the spectrum of pure chitosan powder peaks at 1660 cm\(^{-1}\) and the amine (NH\(_2\)) band at 1591 cm\(^{-1}\), Fig. 1a(i). In Fig. 1a(ii), the carboxamide band has shifted to 1650 cm\(^{-1}\) and the amine band to 1557 cm\(^{-1}\) in the pure chitosan film. 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 [48]. Majid and Arof [49] reported that the amine band in the spectrum of the pure chitosan film is situated at 1553 cm\(^{-1}\) and their results are also comparable with the present work. The shift in these bands as depicted in the spectrum of the chitosan film is attributed to some interactions between the acetic acid solvent and the nitrogen donors of chitosan polymer [48]. The hydroxyl band in the spectrum of pure PVA powder is shown in Fig. 1b(i) at 3354 cm\(^{-1}\). The hydroxyl band in the spectrum of PVA film shown in Fig. 1b(ii) has shifted to 3343 cm\(^{-1}\) indicating that interaction between PVA and the solvent. The hydroxyl band is located at 3337 cm\(^{-1}\) in the spectrum of PVA–chitosan blend film, Fig. 1b(v). Zhang et al. [50] suggested that hydrogen bonds occurred 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.

3.2. Interactions between chitosan–NH\(_4\)NO\(_3\)

Fig. 2a shows the spectra of chitosan–NH\(_4\)NO\(_3\) complexes in the region of hydroxyl band. From the literature [50], the hydroxyl band of chitosan has been reported to be between 3200 and 3500 cm\(^{-1}\). From Fig. 2a(iii), it can be seen that the hydroxyl band in chitosan also experienced some shift on the addition of NH\(_4\)NO\(_3\) salt from 3354 to 3348 cm\(^{-1}\). The \(v_{as}(NH_4^+)\) vibration mode appears...
at 3255 cm\(^{-1}\) with the addition of 50 wt.% \(\text{NH}_4\text{NO}_3\) salt to the polymer, Fig. 2a(iv). In addition, a peak attributed to \(v_s(\text{NH}_4^+)^-\) appears at 3096 cm\(^{-1}\) in the spectrum for the sample with 50 wt.% salt, Fig. 2a(iv). From Chintapalli et al. [51] in the spectrum of PEO–\(\text{NH}_4\text{CF}_3\text{SO}_3\) the \(v_{as}(\text{NH}_4^+)^-\) and \(v_s(\text{NH}_4^+)^-\) modes appear at 3222 and 3097 cm\(^{-1}\) respectively. According to the authors, the symmetry of \(\text{NH}_4^+\) is lowered which in turn reflects interaction between \(\text{NH}_4^+\) and the polymer in their system. Their result is comparable with the present work, thus it is also concluded that chitosan have interacted with \(\text{NH}_4\text{NO}_3\) at the hydroxyl band. In the present work the amine band of pure chitosan film appears at 1557 cm\(^{-1}\) and the carboxamide band at 1650 cm\(^{-1}\) as shown in Fig. 2b(i). On addition of 20 wt.% \(\text{NH}_4\text{NO}_3\) salt, Fig. 2b(ii) the carboxamide and amine bands have shifted to 1644 and 1550 cm\(^{-1}\). The bands shift to even lower wavenumbers as more salt is added and when 50 wt.% of \(\text{NH}_4\text{NO}_3\) was added to chitosan, Fig. 2b(v), the carboxamide and amine peaks shift to 1635 and 1533 cm\(^{-1}\). This indicates that complexation between chitosan and \(\text{NH}_4\text{NO}_3\) has occurred as reported by Majid and Arof [49]. The conducting species in this work is \(\text{H}^+\). This is based on the work by Hashmi et al. [52] that the conducting species in the PEO–\(\text{NH}_4\text{ClO}_4\) complex is the \(\text{H}^+\) ion which originates from the ammonium ion and the conduction occurs via the Groththus mechanism. Buraidah et al. [53] have inferred that in the chitosan–\(\text{NH}_4\text{I}\) complex the cation from \(\text{NH}_4\text{I}\) coordinates with the \(\mathrm{N}\) atom of the amine group in chitosan. \(\text{NH}_4^+\) cations have tetrahedral structure. One of the four hydrogen atoms in \(\text{NH}_4^+\) ions is most weakly bound and can dissociate easily under the influence of an electric field. This \(\text{H}^+\) ion can hop from one site to another leaving a vacancy which will be filled by another \(\text{H}^+\) ion from a neighboring site [52–53]. 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 Groththus mechanism. Fig. 2c represents the spectra of the symmetric \(v_s(\text{NO}_3^-)^-\) vibration mode. From the spectrum in Fig. 2c(vi), the \(v_s(\text{NO}_3^-)^-\) mode of pure \(\text{NH}_4\text{NO}_3\) salt is at 828 cm\(^{-1}\). Liu et al. [54] reported that a symmetric bending band of \(\text{NO}_3^-\) in the spectrum of aqueous \(\text{NH}_4\text{NO}_3\) is situated at 830 cm\(^{-1}\) and the mode is infrared active and their result is comparable with the present work. It can be observed that with increasing amount of \(\text{NH}_4\text{NO}_3\), the intensity of the \(v_s(\text{NO}_3^-)^-\) mode peak increases and it did not shift to lower or higher wavenumbers, Fig. 2c(ii)–(v). Hence it can be concluded that \(\text{NO}_3^-\) anions did not complex with the polymer host in the present work.

3.3. Interactions between PVA–\(\text{NH}_4\text{NO}_3\)

In the present work, the stretching vibration of hydroxyl groups (\(\nu(\text{OH})\)) in the spectrum of pure PVA film appears at 3343 cm\(^{-1}\), Fig. 3a(i). On addition of 30 wt.% of \(\text{NH}_4\text{NO}_3\) salt, the band shifts to lower wavenumbers at 3272 cm\(^{-1}\), Fig. 3a(iv). With further addition of 50 wt.% salt, a new peak attributable to \(v_{as}(\text{NH}_4^+)^-\) and \(v_s(\text{NH}_4^+)^-\) modes of \(\text{NH}_4\text{NO}_3\) salt appear at 3253 and 3086 cm\(^{-1}\), Fig. 3a(viii) implying that interaction occurs between the \(\text{NH}_4^+\) and PVA. From Fig. 3(b), it can be observed that with increasing amount of \(\text{NH}_4\text{NO}_3\), the intensity of the \(v_s(\text{NH}_4^+)^-\) mode peak increases and did not shift inferring that \(\text{NO}_3^-\) anions did not complex with the PVA in the present work. Hema and co-workers have reported that conduction occurs via the O–H group following the Groththus mechanism in PVA–\(\text{NH}_4\text{Br}\) [47] and PVA–\(\text{NH}_4\text{I}\) systems [55].

3.4. Interaction between PVA–chitosan–EC

Fig. 4(a) and 4(b) represents the infrared spectrum of pure PVA–chitosan blend and PVA–chitosan blend films with the addition of EC in the region between 2990 and 3590 cm\(^{-1}\) and 1605 and 1685 cm\(^{-1}\) respectively. It can be concluded that there is no interaction between PVA–chitosan blend and ethylene carbonate since there are no shift of the bands observed in the spectra.

3.5. Interactions between \(\text{NH}_4\text{NO}_3–\text{EC}\)

Fig. 5 shows the infrared spectrum of pure EC and EC mixed with \(\text{NH}_4\text{NO}_3\). To study the interactions between EC and \(\text{NH}_4\text{NO}_3\), EC was heated to 38 °C until it melts and becomes a liquid solution. 0.5 and 1.1 wt.% of \(\text{NH}_4\text{NO}_3\) was added to 50 ml of EC separately and stirred until complete dissolution. From Fig. 5, it can be clearly seen that the C=O bending band which appears in pure EC at 715 cm\(^{-1}\) (Fig. 5a(i)) has shifted to 717 cm\(^{-1}\) (Fig. 5a(ii)) after the addition of 0.5 wt.% \(\text{NH}_4\text{NO}_3\) and to 719 cm\(^{-1}\), Fig. 5a(iii) on the addition of 1.1 wt.% \(\text{NH}_4\text{NO}_3\). In the work of Osman and Arof [48], the shift of the C=O bending band in pure EC was reportedly due to the interaction between \(\text{Li}^+\) salt and C=O group of the EC molecule and their results are in a good agreement with Chintapalli and Frech [56].
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 NH4NO3 was added. The doublet bands in Fig. 5b represent 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.% NH4NO3, 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 [48] and inferring interaction between salt and EC.

3.6. Interactions between PVA–chitosan–NH4NO3

In the present work, the amine band of pure PVA–chitosan blend film appears at the 1558 cm⁻¹ and the carboxamide band at 1647 cm⁻¹. On addition of 10 wt.% NH4NO3 salt, the carboxamide and amine bands shifted to 1625 and 1516 cm⁻¹ respectively, Fig. 6a(ii). For NH4NO3 concentrations up to 40 wt.%, N–H vibration band is not obvious. When the concentration of salt is greater than 40 wt.%, the N–H band is obvious at 3250 cm⁻¹ compared to 3255 cm⁻¹ observed in the spectrum of pure salt, Fig. 6b(v). It can thus be inferred that either the excess salt did not associate or the ions recombine to form neutral ion pairs that the overall conductivity dropped for salt concentrations greater than 40 wt.%. Mason et al. [57] also reported that higher aggregation would result in fewer available charge carriers that will lead towards the decrease of conductivity of their system, poly(N-methyl-propylenimine)-lithium triflate. XRD and SEM confirm the presence of crystallites [36]. The shifts in the carboxamide, amine and hydroxyl bands indicate that interaction occurred between the PVA–chitosan blend (host) and NH4NO3 (doping salt). NO3⁻ anions clearly did not interact with the PVA–chitosan blend polymer electrolyte where it can be observed that the νs(NO3⁻) mode did not shift as depicted in Fig. 6c.

3.7. Interactions between PVA–chitosan–NH4NO3–EC

The infrared spectra of PVA–chitosan–NH4NO3–EC system are shown in Figs. 7 and 8, in the region of C=O bending band of EC and doublet C=O stretching band of EC respectively. From previous work [36], the highest conducting sample for plasticizer free sample has 40 wt.% NH4NO3 concentration. Different amounts of EC have been added to enhance the conductivity. No peak was observed for the sample with 0 wt.% EC in the region of C=O bending band, Fig. 7a and with addition of 70–80 wt.% of EC the peak appeared and have shifted to lower wavenumbers at 715 cm⁻¹, Fig. 7c.

From Fig. 8a no doublet C=O stretching of EC was observed in the spectrum of the EC free sample. With addition of 40 wt.% EC, a C=O doublet peak was observed at 1777 and 1808 cm⁻¹. The doublet peaks shifted to lower wavenumbers on the addition of 60 wt.% EC. Further addition of 70 wt.% EC has shifted the doublet peaks to even lower wavenumbers at 1774 and 1803 cm⁻¹. The conductivity value for the plasticized system in the previous work was found to have maximum value at 70 wt.% EC concentration. However, after the addition of 80 wt.% of EC, the doublet peak has shifted to 1771 and 1790 cm⁻¹ and the intensity of both peaks has also decreased, Fig. 8e. This peak may indicate the increase in crystallinity of the sample accompanied by the decrement of conductivity as studied from the previous work [36]. Based on these observations, the ion conductivity mechanism for PVA–chitosan–NH4NO3 and PVA–chitosan–NH4NO3–EC systems is proposed as depicted in Fig. 9.

Fig. 8. FTIR spectra for PVA–chitosan–40 wt.% NH4NO3 film with (a) 0 wt.% EC, (b) 40 wt.% EC, (c) 60 wt.% EC, (d) 70 wt.% EC and (e) 80 wt.% EC in the region of C=O stretching band.
From FTIR studies, the PVA–chitosan blend films have a carbboxamide, amine and hydroxyl bands. The ammonium nitrate salt interaction with the PVA–chitosan blend is confirmed from FTIR studies, the PVA–chitosan blend films have a carboxamide, amine and hydroxyl bands. The ammonium nitrate salt interaction with the PVA–chitosan blend is confirmed from FTIR spectroscopy.

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