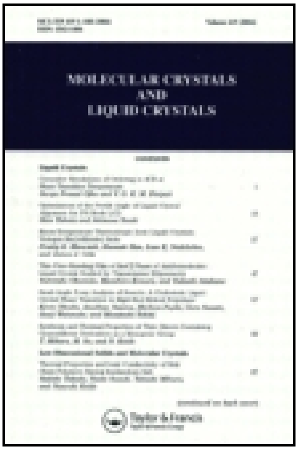

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FTIR Studies of Chitosan-Orthophosphoric Acid-Ammonium Nitrate-Aluminosilicate Polymer Electrolyte

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FTIR Studies of Chitosan-Orthophosphoric Acid-Ammonium Nitrate-Aluminosilicate Polymer Electrolyte

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Complexation between chitosan and orthophosphoric acid is confirmed from the shifting of the carbonyl band in the chitosan acetate spectrum from 1643 cm^{-1} to 1630 cm^{-1} and that of the amine band from 1560 cm^{-1} to 1526 cm^{-1}. H^+ is produced through the dissociation of acid as inferred from the existence of the bands at 1076 and 1159 cm^{-1}. In the spectrum of chitosan-H_3PO_4–NH_4NO_3, a strong peak centered at ~1384 cm^{-1} which can be assigned to the υ(N–O) mode of NO_3^- is observed. The variation in conductivity with Al_2SiO_5 content has been explained in terms of the changes exhibited in the spectra of chitosan-H_3PO_4–NH_4NO_3–Al_2SiO_5.

Keywords: chitosan; conductivity; filler; H_3PO_4; proton conductor

INTRODUCTION

Owing to their complicated structures, the understanding of ionic conduction mechanism in polymer electrolytes is difficult [1]. Polymers are weak electrolytes [2] and ion association can lead to the formation of ion pairs, triplets and multiplets. Therefore information on intermolecular interaction between the components in polymer electrolytes can be an important probe to appreciate and understand the ionic conduction mechanism [3]. These interactions can be investigated by FTIR spectroscopy. Apart from being able to understand the ionic conduction mechanism, this technique has been used to verify the occurrence of complexation in many polymer electrolyte systems.

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Complexation can be inferred from the shifting of polar functional groups and the appearance of peaks other than those of the host materials [4]. In some proton conducting polymer electrolytes, the interaction between acid and solvent can reveal the possibility of protonation of solvent molecules by the acid [5–6]. FTIR can also help to speculate the mechanism of proton conduction in the sample. In the case of chitosan, [7–8], occurrence of complexations in chitosan films can be identified by the shifting of the carbonyl and amine bands. In this article, studies on the interaction between chitosan and its doping materials such as orthophosphoric acid (H_3PO_4), ammonium nitrate (NH_4NO_3) and aluminosilicate (Al_2SiO_5) were carried out using FTIR spectroscopy.

EXPERIMENTAL

Chitosan films were prepared from highly viscous powder procured from Fluka. The relative molecular weight is 600,000. 1 g of chitosan was dissolved in 100 ml of 1% acetic acid (AJAX) solution. Different volume percentage of H_3PO_4 solution were added to different beakers containing the chitosan-acetic acid solution. To prepare chitosan films complexed with NH_4NO_3, the salt was added to the chitosan acetate-H_3PO_4 solution. In the preparation of chitosan based composite samples, different amounts of Al_2SiO_5 were added to the ternary solution containing chitosan, orthophosphoric and NH_4NO_3 and let to dry at room temperature to form films. In this work, infrared studies were carried out using the FTIR Spectrometer Spectrum RX-1 in the wavenumber region between 4000 to 500 cm^{-1}. Resolution 1 cm^{-1}.

RESULTS AND DISCUSSION

Chitosan-H_3PO_4 Spectra

The detailed band assignments for chitosan have already been reported in the literature [7–16]. Figure 1 shows the spectra of pure chitosan acetate in the spectral region from 700 to 4000 cm^{-1}. The description of vibrations in the chitosan acetate was tabulated in Table 1. From the figure the carbonyl and amine bands are located at 1643 and 1560 cm^{-1} respectively.

Figure 2(a) shows the FTIR spectra of chitosan acetate film, 1% H_3PO_4 solution and films containing different weight percentage of chitosan and H_3PO_4. The band around 1151 cm^{-1} in Figure 2(a) is due to the C−O−C antisymmetry stretching in the chitosan ring [15]. The bands at 1074 and 1032 wavenumbers [17] are due to antisymmetry

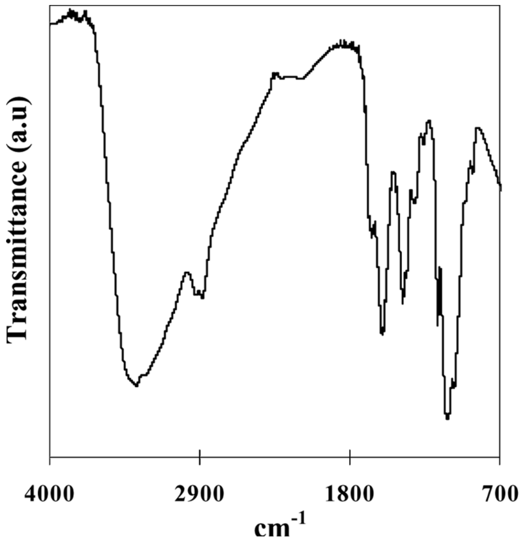

FIGURE 1 Pure chitosan acetate in the 700 to 4000 cm^{-1} spectral region.

of C–OH in chitosan [15,17]. The peak at 1178 cm^{-1} in Figure 2(b) is due to symmetry stretching of P=O [18] in dilute H_3PO_4. The peak at 1076 cm^{-1} is due to symmetry stretching for P–OH of $H_2PO_4^-$ in dilute H_3PO_4 [5]. This infers that in 1% dilute H_3PO_4 solution, the acid has partially undergone two stages of dissociation as follows:

$$H_3PO_4 \rightarrow H_2PO_4^- + H^+$$

and

$$H_3PO_4^- \rightarrow HPO_4^{2-} + H^+$$

TABLE 1 Vibrational Modes and Wavenumbers Exhibited by Chitosan Acetate

Description of vibrations	Wavenumbers (cm^{-1})
O=C–NHR	1643
NH_2	1560
$\delta(CH_2)$	1411
Symmetrical deformation (CH_3)	1387
$\omega(CH_2)$	1344
ν_a (C–O–C)	1153
ν_a (C–O)	1074, 1032

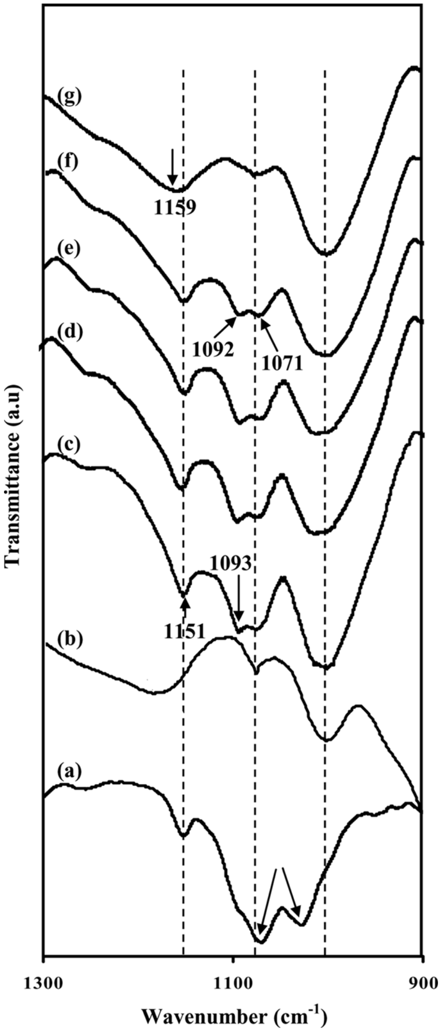

FIGURE 2 IR spectrum of (a) CA (b) H_3PO_4 (c) CA-9 vol.% H_3PO_4 (d) CA-23 vol.% H_3PO_4 (e) CA-33 vol.% H_3PO_4 (f) CA-41 vol.% H_3PO_4 (g) CA-47 vol.% H_3PO_4 in the spectral region from 900 to 1300 cm^{-1}.

The peak around 1000 cm^{-1} in Fig. 2(c) is due to antisymmetry stretching of P–O in H_3PO_4 solution [19]. On addition of diluted H_3PO_4 to chitosan, the peaks at 1074 and 1032 wavenumbers shift to 1093 and 1071 wavenumbers respectively probably due to complexation between the oxygen in C–OH of chitosan with HPO_4^{2-}.

On increase in H_3PO_4 content the two peaks merge to form a broad band that peaks at $1076\,cm^{-1}$, Figure 2 (g). It is to be noted that in this sample the amount of diluted H_3PO_4 solution added was 47 vol.%. Due to the high content of diluted H_3PO_4 only a portion of H_3PO_4 that has dissociated to $H_2PO_4^-$ undergoes a second stage of dissociation to HPO_4^{2-}. A major portion of $H_2PO_4^-$ undergo complexation with the oxygen atom in the C–O–C portion of the chitosan ring explaining the shift of the C–O–C band from $1151\,cm^{-1}$ to $1159\,cm^{-1}$. Gong [20] has also attributed the band at $1155\,cm^{-1}$ to $H_2PO_4^-$

Figure 3 shows the infrared spectra of the same system for wavenumbers ranging from 1450 and $1750\,cm^{-1}$. In Figure 3(a), the chitosan acetate spectrum shows the presence of amino group at $1560\,cm^{-1}$ and the carbonyl group at $1643\,cm^{-1}$. The intensity of amino group is greater than that of the carbonyl group indicating that the chitosan is highly deacetylated. Complexation occurs with the lone pair electron of the nitrogen and oxygen atoms in chitosan. This can be inferred from the spectrum of the sample containing 9 vol.% of H_3PO_4 in which the carbonyl and amino bands have shifted to lower wavenumbers and the intensity of the amino group is slightly lower than the intensity of the carbonyl band. With further addition of H_3PO_4 the amino band has become asymmetrical and the intensity of the spectrum towards $1450\,cm^{-1}$ is almost constant. The transmittance due to the amino group has also decreased while the transmittance due to the carbonyl group has increased and is also broader indicating that complexation with the oxygen heteroatom is more favorable. This is in agreement with Stevens *et al.* [5], where it has been reported that the interaction between H_3PO_4 and DMF occurs via the carbonyl group of DMF.

Chitosan-H_3PO_4–NH_4NO_3 spectra

Figure 4 shows the spectra of CA–H_3PO_4–NH_4NO_3 complexes in the region from $1250\,cm^{-1}$ to $1700\,cm^{-1}$. A strong peak centered at $1384\,cm^{-1}$ is observed in the spectrum of the ternary compound when 5 wt.% salt is added to the binary complex. This band could be assigned to $\nu_3(NO_3^-)$ of NH_4NO_3 salt [21]. The intensity of this peak increases before it splits into two bands at $1383\,cm^{-1}$ and $1396\,cm^{-1}$ respectively (Fig. 4(f)). The presence of these bands at high salt concentration may indicate the presence of multiplet neutral ions which lead to the decrease in number of mobile ions and therefore to the decrease in conductivity.

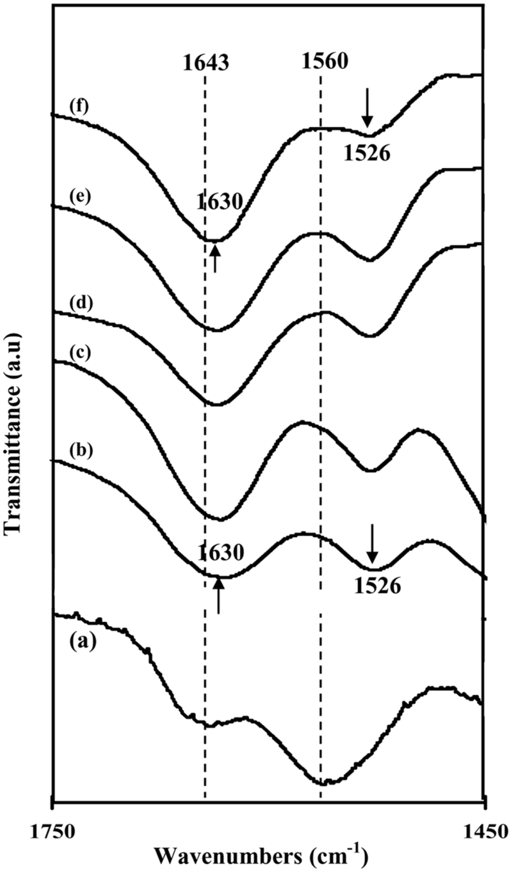

FIGURE 3 IR spectrum of (a) CA (b) CA-9 vol.% H_3PO_4 (c) CA-23 vol.% H_3PO_4 (d) CA-33 vol.% H_3PO_4 (e) CA-41 vol.% H_3PO_4 (f) CA-47 vol.% H_3PO_4 in the spectral region from 900 to 1300 cm^{-1}.

Chitosan-H_3PO_4–NH_4NO_3–Al_2SiO_5 Spectra

Figure 5 shows the spectra of H_3PO_4–NH_4NO_3–Al_2SiO_5 complexes in the region from 1300 to 900 cm^{-1}. The addition of fillers to the ternary salted sample seems to have some effects on the complexation between the polymer and the salt. When 0.3 and 0.5 wt.% Al_2SiO_5 were added to the highest conducting sample in the CA–H_3PO_4–NH_4NO_3 system, a bigger portion of the fixed amount of NH_4NO_3 form complexes with the polymer. This led to the increase in intensity of the amine and carbonyl band. Hence the number of free NH_4^+ and NH_3^- ions decrease.

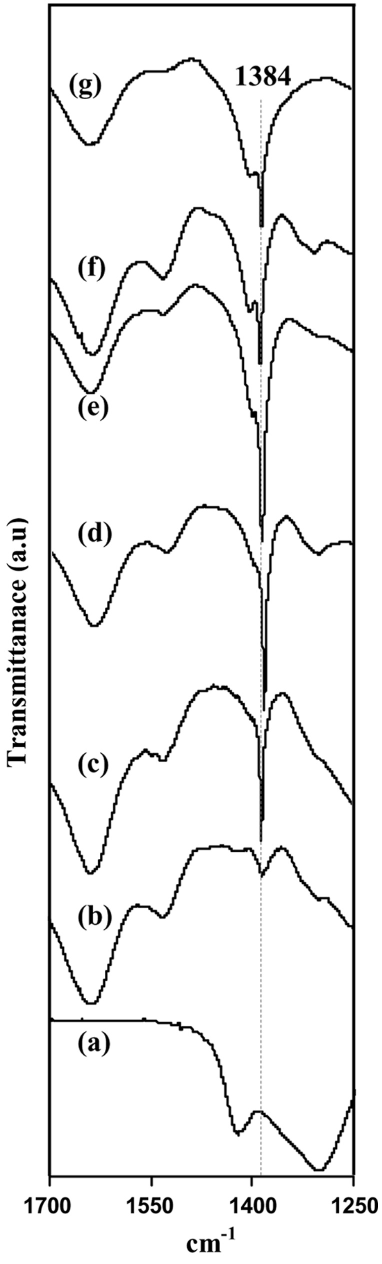

FIGURE 4 IR spectrum of (a) NH_4NO_3 and (b) CA$-H_3PO_4$ with various concentration of NH_4NO_3 of (c) 5 wt.% (d) 10 wt.% (e) 15 wt.% (f) 20 wt.% (g) 25 wt.% in the 1250 cm^{-1} to 1750 cm^{-1} spectral region.

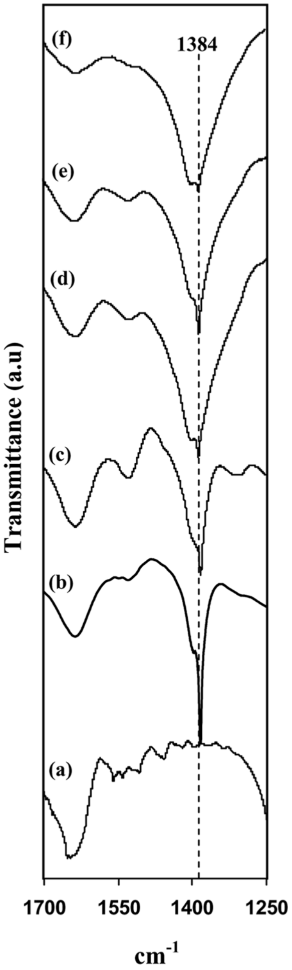

FIGURE 5 IR spectrum of (a) Al_2SiO_4 (b) CA–H_3PO_4-15 wt.% NH_4NO_3 and CA–H_3PO_4–NH_4NO_3–Al_2SiO_4 with various concentration of Al_2SiO_4 of (c) 0.5 wt.% (d) 0.8 wt.% (e) 1.3 wt.% (f) 3.0 wt.% in the 1250 cm^{-1} to 1700 cm^{-1} spectral region.

The increase in intensity of the carbonyl and amino bands is greater in the spectrum of the ternary sample added with 0.5 wt.% Al_2SiO_5. This is supported by the decrease in conductivity for the 0.3 wt.% and a further decrease in conductivity for the 0.5 wt.% fillered ternary sample, Figure 6. This decrease is real since the error bars in the conductivity plot do not overlap. In the spectrum of the film with

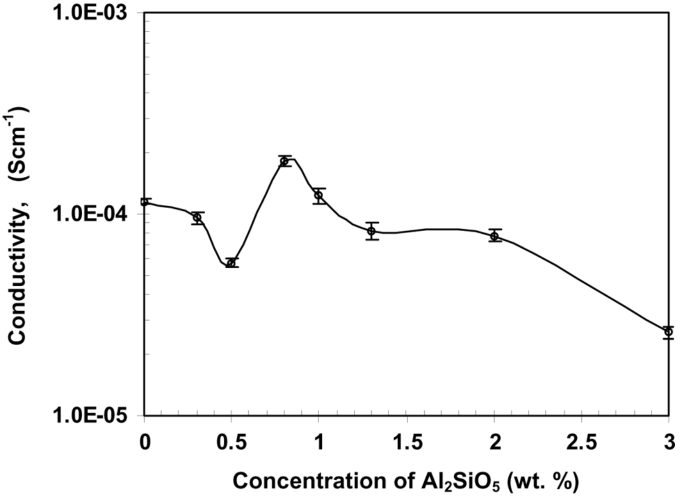

FIGURE 6 Effect of Al_2SiO_5 concentration on the conductivity of $CA-H_3PO_4-NH_4NO_3-Al_2SiO_5$ system.

0.8 wt.% filler, a lesser amount of salt participated in the complexation with the polymer and the intensity of the carbonyl and amine bands decreased. The number density of mobile ions should therefore increase and this is also evident from the increase in intensity of the ν(N–O) mode of NO_3^- at 1384 cm^{-1}. This is manifested in the increase in conductivity of the film containing 0.8 wt.% Al_2SiO_5. The decrease in conductivity for the samples with 1.0, 1.3, 2.0 and 3.0 wt.% Al_2SiO_5 is attributed to the formation of neutral $NH_4NO_3-Al_2SiO_5$ complexes as can be inferred from the disappearance of the amino band and the broadening of the 1384 cm^{-1} band in Figure 5(f).

CONCLUSION

FTIR has shown the peaks that can be attributed to $H_2PO_4^-$ and HPO_4^{2-} at ~1150 cm^{-1} and ~1076 cm^{-1} respectively. This shows that the conducting species is H^+. Complexation occurs between the acid and the carbonyl and amino groups of the polymer, but the tendency is more favorable between the acid and the carbonyl group. The interaction of NH_4NO_3 with chitosan and H_3PO_4 is evidenced with the presence of the peak at 1384 cm^{-1}. The addition of more than 0.8 wt.% Al_2SiO_5 lowers the conductivity and this has been attributed to the formation of neutral moieties that do not contribute to the conductivity.

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