

X-ray diffraction studies of chitosan acetate-based polymer electrolytes

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ABSTRACT Chitosan is the product when partially deacetylated chitin dissolves in dilute acetic acid. This paper presents the x-ray diffraction patterns of chitosan acetate, plasticized chitosan acetate and plasticized-salted chitosan acetate films. The results show that the chitosan acetate-based polymer electrolyte films are not completely amorphous but it is partially crystalline. X-ray diffraction study also confirms the occurrence of the complexation between the chitosan and the salt and the interaction between salt and plasticizer. The salt-chitosan interaction and salt-plasticizer interaction is clearly justified by infrared spectroscopy.

(XRD, Chitosan, Ethylene carbonate, Lithium triflate, Complexation)

INTRODUCTION

In order to find alternative polymer to act as an electrolyte in solid-state polymer batteries, chitosan was studied [1-3]. Chitosan is a polymer of β -1,4-linked 2-amino-2-deoxy-D-glucopyranose. It can be derived by deacetylation of chitin or obtained from the cell walls of living things such as *phycomyces blakesleeanus*. It is non-toxic, odorless, and biocompatible in animal tissues, enzymatically biodegradable and has variety of uses [4-7]. It has an amine group (NH_2) and the nitrogen atoms have lone pair electrons that can act as electron donors and can interact with inorganic salts. Interaction between a lithium-cation and nitrogen donor has been proven by x-ray photoelectron spectroscopy [8].

Polymers are known to exhibit crystalline and amorphous phases. Thus x-ray diffraction studies on polymers will confirm the degree of crystallinity or amorphicity. In the present work, x-ray diffraction technique will be used to prove complexation between chitosan and the lithium triflate and to investigate the effect of the plasticizer, ethylene carbonate (EC) on the chitosan acetate-based polymer electrolytes.

EXPERIMENTAL

Sample Preparation

1 g of chitosan (6×10^5 g/mol, Fluka) was dissolved in 100 ml 1% acetic acid solution. Lithium triflate (LiCF_3SO_3) and ethylene carbonate (EC) were added accordingly. After complete dissolution, the solutions were cast in petri dishes and left to form films of pure chitosan acetate (CA), CA-EC, CA- LiCF_3SO_3 and CA-EC- LiCF_3SO_3 at room temperature. Pure chitosan film was prepared by immersing the CA film in NaOH solution and then continuously washed with distilled water. The films were then transferred into a dessicator for continuous drying.

X-Ray Diffraction Measurements

X-ray diffraction was carried out using the Siemens D-5000 X-Ray Diffraction system. In this method, when x-rays hit a sample, some of the rays are diffracted. These films were adhered onto cleaned microscope slides and then placed in the sample chamber around which a detector is moved. As the sample rotates, the angle θ between the incident beam and the normal to the film is changed. X-rays are reflected to the detector when the Bragg condition

$$2d\sin\theta = n\lambda \quad (1)$$

is fulfilled. Here d is the interplanar spacing, θ , the Bragg angle, n is the order of reflection and λ is the x-ray wavelength. The samples were scanned with a beam of monochromatic $\text{CuK}\alpha$ -X-radiation of wavelength $\lambda = 1.5406 \text{ \AA}$ between a 2θ angle of 5° to 40° . In order to estimate the degree of crystallinity or amorphicity, the Scherrer length can be calculated using the equation,

$$L = \frac{0.9\lambda}{\Delta 2\theta_b \cos \theta_b} \quad (2)$$

Here θ_b is glancing angle, λ is the wavelength of x-rays and $\Delta 2\theta_b$ is the difference in angle at the two ends of the Full Width at Half Maximum (FWHM).

FTIR Spectroscopy Measurements

Infrared spectra exhibited in this work were taken with a MAGNA-IR550 Spectrophotometer-Series II in the wavenumber region between 4000 to 400 cm^{-1} . The films used in this work were about 0.01 mm thickness, cut in suitable sizes and placed in the specimen holder of the spectrophotometer. The spectra shown in this paper was the result of 20 scans at the speed of 1 scan per 2 seconds.

RESULTS AND DISCUSSION

In this work, the x-ray diffraction patterns of chitosan and chitosan acetate films show peaks at $2\theta = 9.41^\circ$, 14.55° and 20.58° . This result shows that chitosan and chitosan acetate films are still partially crystalline and in well agreement with the result reported by Sakurai and co-workers [9-10]. Fig.1 represents the x-ray diffraction patterns of chitosan acetate and plasticized chitosan acetate films. It can be observed that the x-ray diffraction patterns are the same. The crystalline peaks are still observed at $2\theta = 9.41^\circ$, 14.55° and 20.58° . Fig.1 (inset) shows the x-ray diffraction patterns of pure ethylene carbonate. High intensity peaks can be observed at $2\theta = 17.2^\circ$, 20.0° and 26.6° . The peaks of plasticized chitosan acetate films are observed unchanged even after the addition of 41 wt % ethylene carbonate to the film. The peaks due to the ethylene carbonate are not observed in x-ray

diffraction patterns of plasticized chitosan acetate films. These results show that ethylene carbonate does not interact chemically with chitosan acetate.

Fig. 2 shows the x-ray diffraction patterns of the salted chitosan acetate films. Fig. 2 (inset) shows the x-ray diffraction pattern of the pure salt (lithium triflate). It can be seen that as the salt content increases, the crystalline peak at $2\theta = 20.48^\circ$ shift towards lower 2θ angles. Within the range $13^\circ \leq 2\theta \leq 25^\circ$, there are many peaks attributable to the salt. So, the crystalline peak shifts towards lower 2θ angles towards region where the salt exhibits its fingerprint. With the amount of salt added from 0.1 g to 0.5 g , apart from shifting to lower 2θ angles the x-ray diffraction patterns are still quite symmetrical. When 0.6 g of salt was added the crystalline peak shifts towards lower 2θ angles but the x-ray diffraction pattern shows some distortion from symmetry. When 0.7 g salt was added the crystalline peak shifts back towards larger 2θ angles but the noise level is also observed to increase. The x-ray diffraction patterns again preserved the crystalline peak in symmetrical nature when 0.8 g to 1.0 g of salt has been added. The addition of salt can also increase the amorphicity of the films. There is an optimization concentration of salt after which on increasing amounts of salt added, the samples tend to become more crystalline. This indicates that complexation has occurred between the metal salt and chitosan or the metal salt is said to have chelated to the chitosan acetate polymer.

Infrared spectroscopy also confirms salt-polymer complexation with the shifting of the amine bands. Fig. 3 shows the infrared spectrum of salted-chitosan acetate films. It can be observed that the amine bands at 1590 cm^{-1} and 1650 cm^{-1} have shifted to lower wavenumbers and ends looking like one broad band at high salt concentrations.

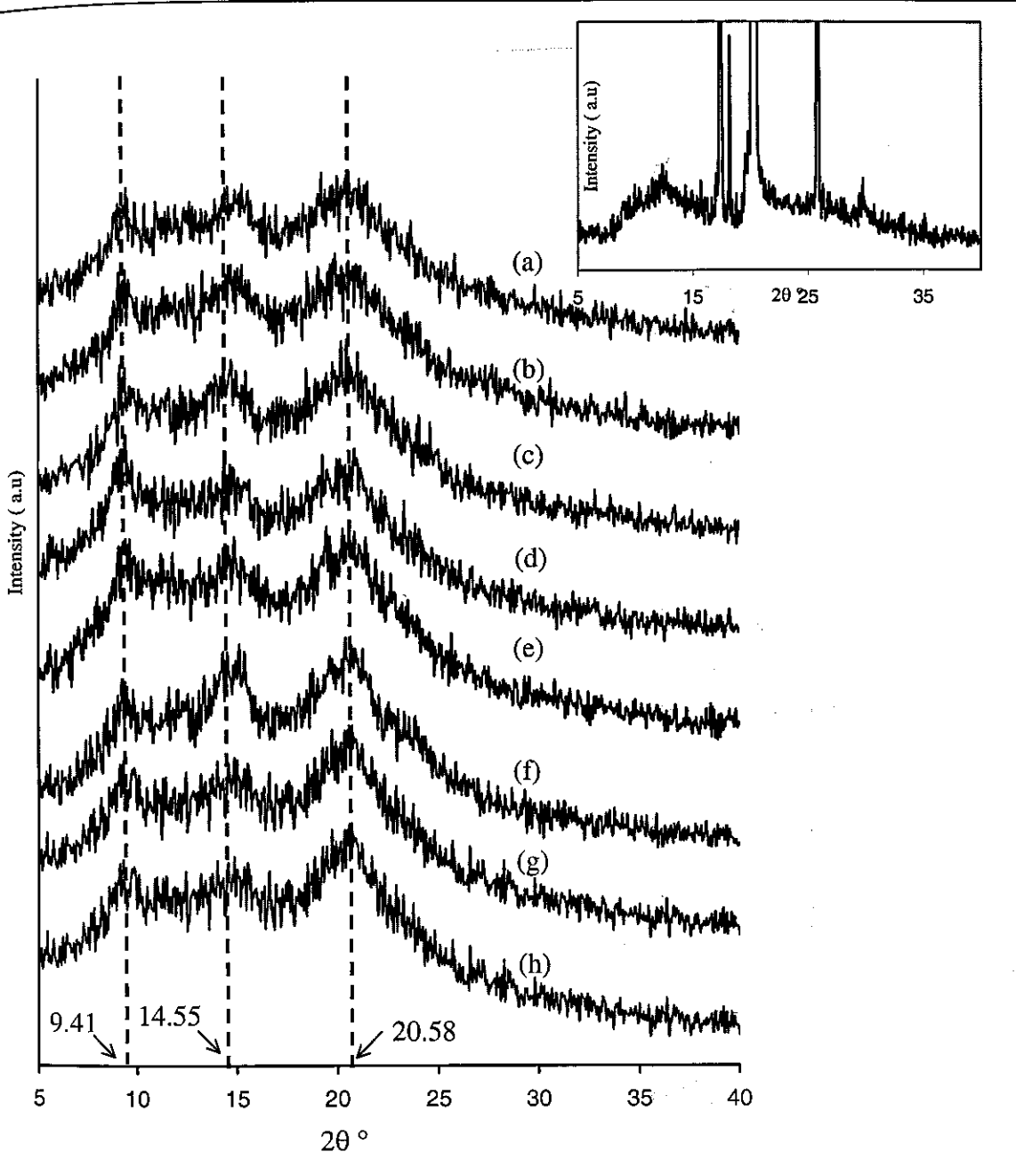


Figure 1. X-ray diffraction patterns of (a) chitosan acetate (CA) film and plasticized CA films with various concentrations of EC (in grams)(b) 0.1 (c) 0.2 (d) 0.3 (e) 0.4 (f) 0.5 (g) 0.6 (h) 0.7 and x-ray diffraction pattern of ethylene carbonate (inset).

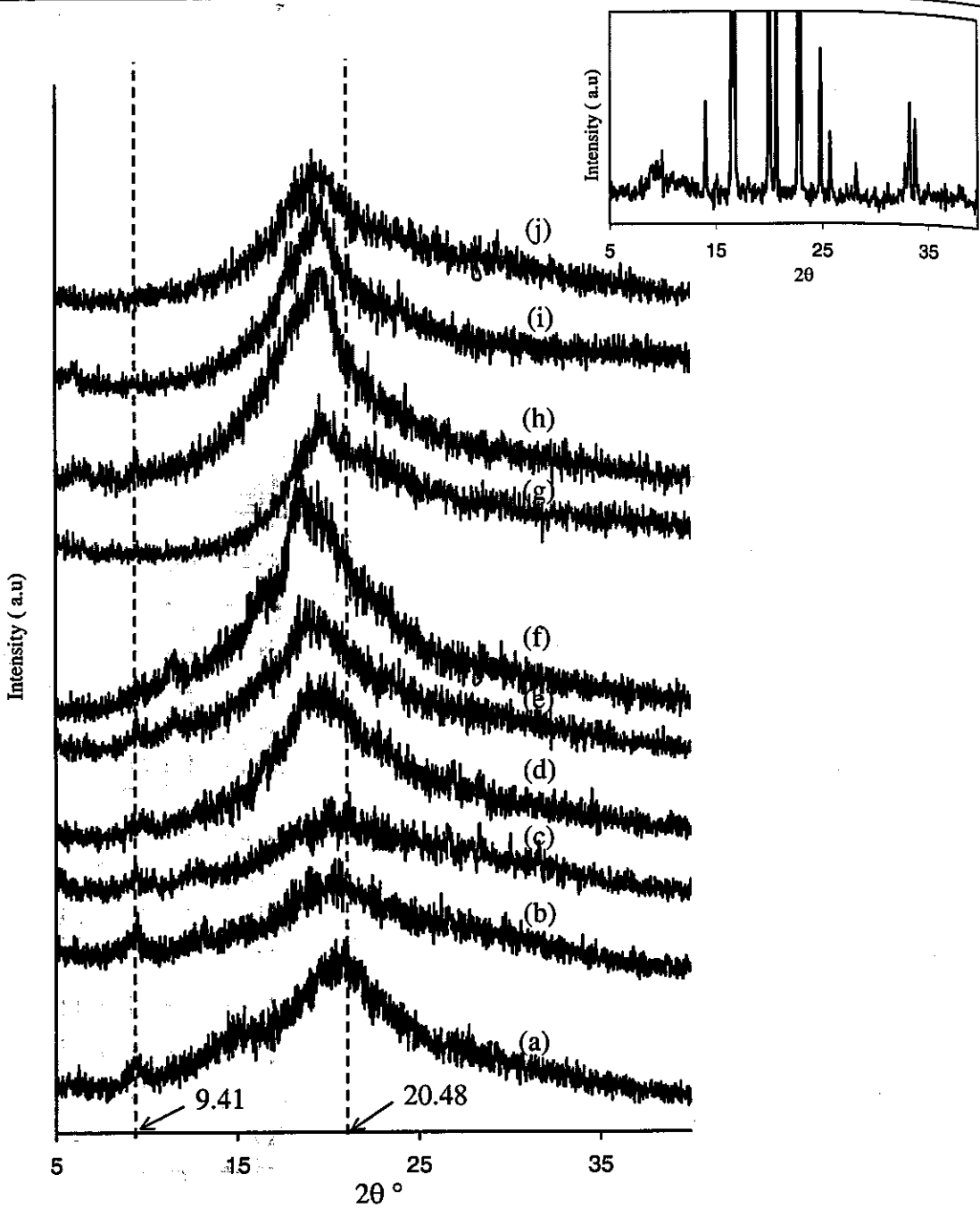


Figure 2. X-ray diffraction patterns of salted chitosan acetate films with various concentrations of salt (in grams) (a) 0.1 (b) 0.2 (c) 0.3 (d) 0.4 (e) 0.5 (f) 0.6 (g) 0.7 (h) 0.8 (i) 0.9 and (j) 1.0 and x-ray diffraction pattern of lithium triflate (inset).

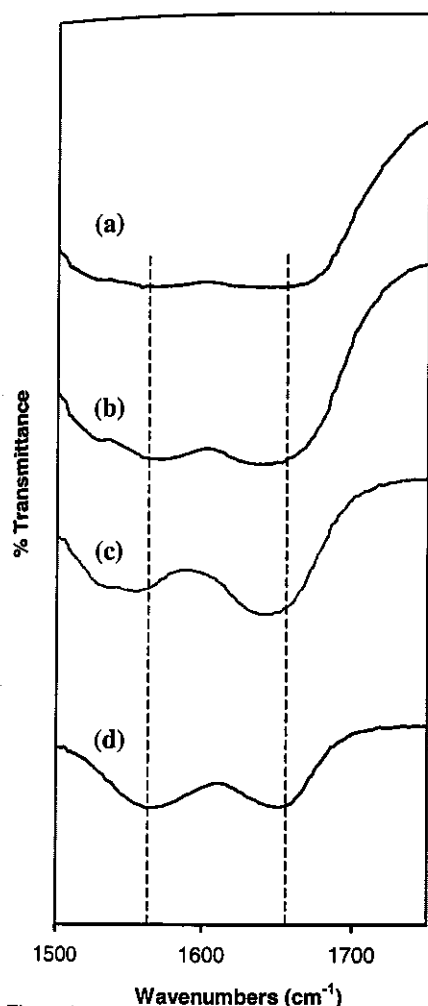


Figure 3. The FTIR spectra of (a) Pure CA and CA with (b) 10 wt% LiCF₃SO₃ (c) 23 wt% LiCF₃SO₃ (d) 33 wt% LiCF₃SO₃.

Fig. 4 depicts the x-ray diffraction patterns of plasticized salted films. In these films the amount of salt is kept constant. It can be seen that on addition of 5 wt%, 10 wt% and 20 wt% of ethylene carbonate, two peaks are observed at $2\theta = 11.18^\circ$ and $2\theta = 17.94^\circ$. These peaks may represent a new phase as a result of interaction between the salt and polymer as mentioned above and may also be due to salt and plasticizer interaction. These peaks decrease in intensity, as the ethylene carbonate content is increased. The films with high ethylene carbonate content from 30 wt% to 50 wt% have high degree of amorphicity. This is also verified by the Scherrer lengths calculated for the plasticized salted-chitosan acetate films measured at the 2θ angles representing the crystalline peak. This is tabulated in Table 1.

Table 1: Scherrer length for salted chitosan acetate films with various concentrations of plasticizer.

EC content (wt%)	Scherrer length (Å)
5	16.4
10	16.2
20	15.8
30	15.2
40	14.5
50	14.0

The Scherrer lengths seem to decrease with increasing plasticizer content. This could be due to the interaction between the salt and the plasticizer. Ethylene carbonate has an oxygen atom that is doubly bonded to a carbon atom and two other oxygen atoms in its structure, which has lone pair electrons. It is known that hard cations such as Li⁺ prefer to form dative bonds with the oxygen atom rather than the nitrogen atom in the amine group of chitosan [11]. The Li⁺ ion prefers to bond with the oxygen atom of the EC and as the EC content increases, the Li⁺ ions will form bonds with more oxygen atoms. This reduces complexation between Li⁺ ions and nitrogen atoms thus making the material more amorphous and the Scherrer length decreases. The interaction between salt and plasticizer can also be observed in infrared spectrum as shown in Fig. 5.

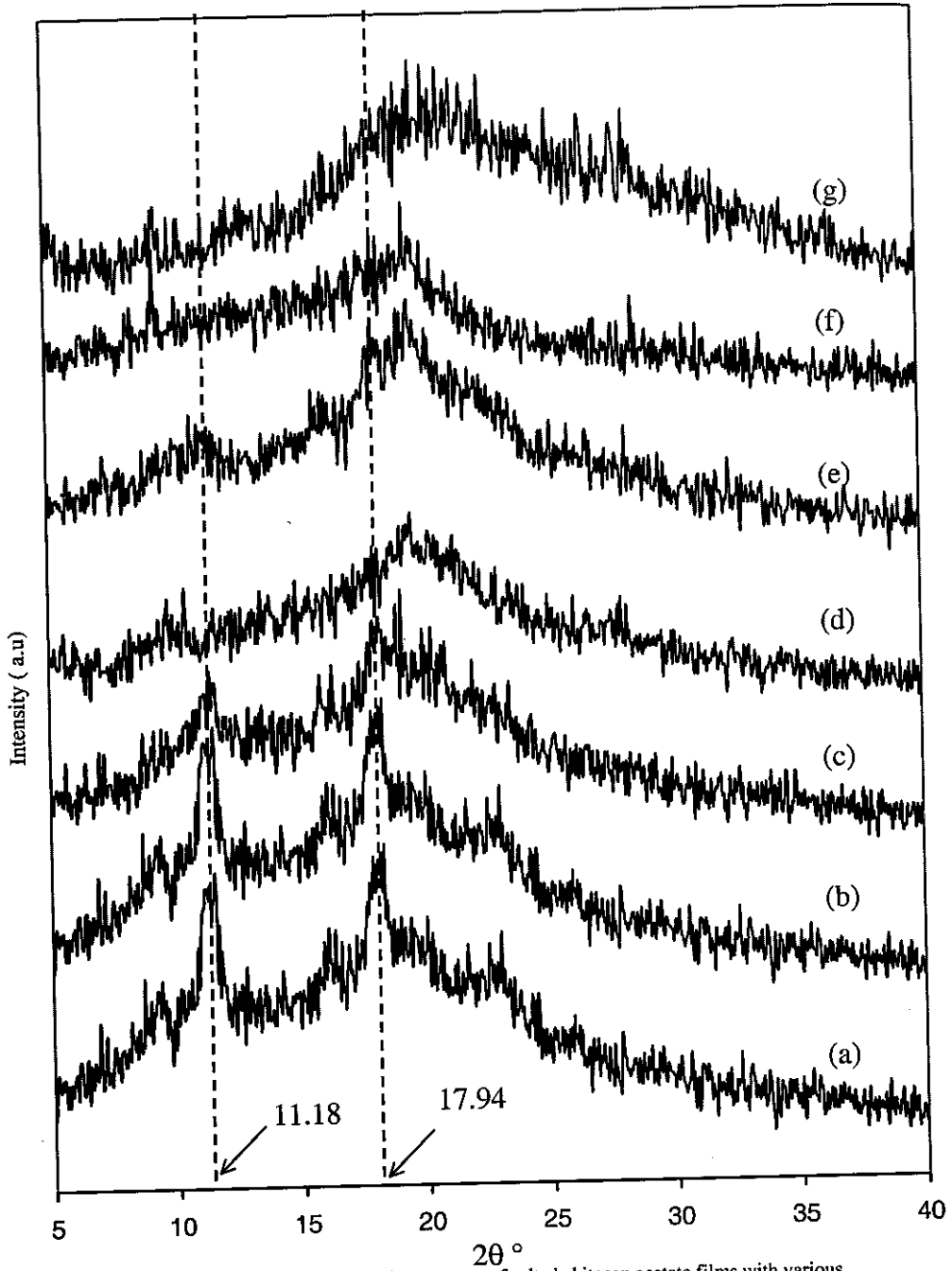


Figure 4. X-ray diffraction patterns of salted chitosan acetate films with various concentrations of plasticizer (in wt%) (a) 5 (b) 10 (c) 20 (d) 30 (e) 40 (f) 50 and (g) salted CA film without plasticizer.

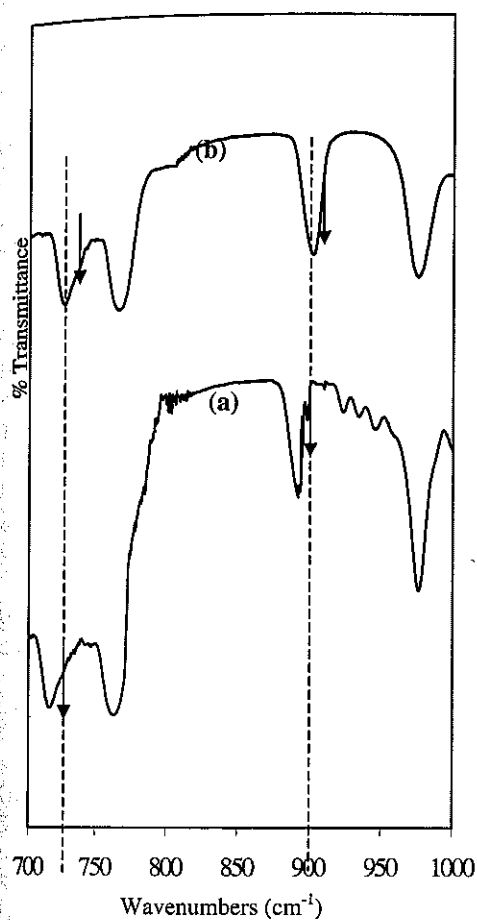


Figure 5. Infrared spectrum of (a) pure EC (b) EC-LiCF₃SO₃.

The band at 718 cm⁻¹ in the spectrum of pure EC has shifted to 725 cm⁻¹ in the spectrum of EC-LiCF₃SO₃. The band at 718 cm⁻¹ is assigned to C=O bending. The Li⁺-EC interaction is also evident in the ring breathing region at 893 cm⁻¹ in the pure EC spectrum, which has shifted to 898 cm⁻¹ in the EC-LiCF₃SO₃ spectrum. Others researchers [12-13] have also reported Li⁺ interaction with oxygen atom in propylene carbonate and ethylene carbonate. This strengthens the inference of salt-EC interaction from x-ray diffraction studies as illustrated by the x-ray patterns of Fig. 4.

CONCLUSIONS

X-ray diffraction study shows that the chitosan acetate-based polymer electrolyte films are not completely amorphous polymer but it is partially crystalline. X-ray diffraction study also confirms the occurrence of the complexation between the chitosan and the salt and the interaction between salt and plasticizer. These results are clearly justified by infrared spectroscopy.

Acknowledgements ZO would like to thank the Ministry of Science, Technology and Environment for the scholarship awarded and AKA and ZAI thanks the government of Malaysia for the vote 03-02-03-0423.

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