

## Evidence of complexation between plasticized argentum triflate and chitosan by x-ray photoelectron spectroscopy (XPS)

M.M. Ali<sup>1</sup>, M.Z.A. Yahya<sup>1</sup>, R. Puteh<sup>2</sup>, F. Sonsudin<sup>2</sup>, R. Yahya<sup>3</sup>, M.A. Yarmo<sup>4</sup> and A.K. Arof<sup>5</sup>

<sup>1</sup> Physics Department, Faculty of Applied Science, MARA University of Technology, 40450 Shah Alam, Selangor, Malaysia.

<sup>2</sup> Center for Foundation Studies, University of Malaya, 50603 Kuala Lumpur, Malaysia.

<sup>3</sup> Chemistry Department, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia.

<sup>4</sup> School of Chemical Science and Food Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia.

<sup>5</sup> Physics Department, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia.

**ABSTRACT** Chitosan with a molecular weight of  $6 \times 10^5$  g mol<sup>-1</sup> was used in this study. Chitosan is doped with silver triflate (AgCF<sub>3</sub>SO<sub>3</sub>) to produce an ion-conducting polymer that can be used as an electrolyte in solid-state electrochemical cells. Ethylene carbonate (EC) was added to enhance electrical conductivity. The polymer film was prepared by the solution cast technique. X-ray diffraction (XRD) confirms the disruption of the crystalline order of plasticized chitosan upon complexation and their conversion to the amorphous state for samples that exhibit increasing electrical conductivity. Complexation is confirmed by x-ray photoelectron spectroscopy (XPS) whereby the signal peak ranging from 375.9 to 376.6 eV is attributable to Ag-N interaction.

(Chitosan, Argentum triflate, XRD, XPS)

### INTRODUCTION

The development of organic and polymeric conducting materials is of great scientific and commercial interests. The importance of ionic motion in solvent free polymeric matrices has been recognized for more than two decades now. While polyelectrolytes, i.e. polymeric backbones with attached ionized groups are of considerable theoretical and practical importance; they are conductive only in the presence of polar solvents. Their electrochemical properties are limited by the solvent and the conductivity takes place via interconnecting blocks of solvent containing ions, the structure of which is quite similar to that of free solutions. Polymer electrolytes correspond to a different concept: the polymer itself acts as solvent for the salt which becomes partially dissociated in the matrix, leading to ionic conductivity. No solvent is required for the conduction process though the preparation of the polymer-salt complex involves the use of a solvent for both constituents.

Complexation between a polymer and a salt is possible due to the existence of polar groups in polymers. These polar groups can act as electron donors. These electron donors will form a dative bond with the cation of the salt. A cation can be "hard" or "soft". A hard cation is non-polarizable. The Li<sup>+</sup> ion is an example of a hard cation. Soft cations are those having partially filled "d" or to a lesser extent "f" orbital. For non-polarizable cations the most suitable polymers are those with oxygen donors followed by those having secondary nitrogen (NH) and sulphur donors. For salts with soft cations the more preferred polymer is one that contains secondary nitrogen. Tertiary nitrogen (=N-) usually shows steric restriction. This is followed by polymers containing sulphur and oxygen donors. Complexation is highly facilitated when the geometry of the ligand is pre-arranged to form cyclic structures where the ion is part of a 5-, or a 6- membered ring [1]. The presence of large delocalized anions, either "soft" (I<sup>-</sup>) or "hard" bases (ClO<sub>4</sub><sup>-</sup>), require little solvation. The

order is  $\text{Cl}^- < \text{Br}^- < \text{I}^- \approx \text{SCN}^- < \text{ClO}_4^- \approx \text{CF}_3\text{SO}_3^- < \text{AsF}_6^-$ .

It is the aim of this study to use chitosan as the polymer host due to the presence of the amine group in the polymer. The salt is  $\text{AgCF}_3\text{SO}_3$  (silver triflate), which contains a "soft" cation. Complexation will be proven by x-ray photoelectron spectroscopy (XPS). To enhance the conductivity the polymer-salt complex will be plasticized with ethylene carbonate (EC). The plasticized chitosan acetate-silver triflate complexes will be prepared by the solution cast technique. The film will be characterized by x-ray diffraction (XRD) to study the effect of the dissolution of the salt on the structure of the polymer. X-ray photoelectron spectroscopy will also be carried out to confirm that the shift in XRD peaks is due to Ag-N interaction.

## EXPERIMENTAL

### Sample Preparation

Chitosan powder used in the present investigation was obtained from FLUKA. All samples were prepared by the solution cast technique. Chitosan with  $6.0 \times 10^5 \text{ g mol}^{-1}$  molecular weight was used. A stock solution of composition 1.0 g chitosan in 100 ml 1% of acetate acid was prepared. The inorganic salt, recrystallized silver triflate ( $\text{AgCF}_3\text{SO}_3$ ) was taken in different stoichiometric ratios and dissolved in the stock solution. The mixtures were continuously stirred with a magnetic stirrer for several hours at room temperature to ensure complete dissolution of the salt. The prepared solutions were then cast into different plastic petri dishes and films were allowed to form at room temperature. The films were formed after about several weeks. The resulting films were then kept dry in a dessicator for further experiments.

### X-ray Photoelectron Spectroscopy (XPS)

The XPS studies in this work were carried out using a Kratos XSAM HS surface analysis spectrometer with an Mg  $K_{\alpha}$  x-rays source that produces 1253.6 eV x-ray. This spectrometer is available at Universiti Kebangsaan Malaysia. The spectrometer was calibrated using a clean Ag plate and the Ag  $3d_{5/2}$  line was set at 368.25 eV. The survey scan was taken for binding energies between 10 eV - 1100 eV. The pass energy and step size energy were 160 eV and 1 eV per step respectively. Sweep time was set at 300 seconds. For the narrow scan, a smaller pass energy 20 eV with lower step size energy of 0.1 eV per step were used and the sweep time was 59.898 seconds per sweep. The software version provided by Kratos deconvoluted all core-level spectra into their gaussian component peaks. Charging effect was corrected using the C 1s binding energy at 284.5 eV was used. The assignments of the binding energy peaks were based from the Handbook of X-ray photoelectron spectroscopy [2].

## RESULTS AND DISCUSSION

To prove complexation between silver triflate and the chitosan polymer, XPS analysis was sought for. The binding energy of the Ag 3d and N 1s core level electrons will have to be determined for the above objective. It was possible to deconvolute the silver core-level spectrum into two gaussian component peaks (Figures 1 to 3), one peak at the binding energy corresponding to the Ag-N interaction and the other peak for the  $\text{Ag-CF}_3\text{SO}_3$  binding energy. Likewise, it was possible to deconvolute the core-level N spectrum into at most three gaussian component peaks (Figures 4 to 6) that can be assigned to the amine bands, the chitosan-acetate salt and the N-Ag interaction. Table 1 shows the binding energies of the gaussian component peaks in the core-level spectra of N and Ag after charging correction.

Binding energies of the gaussian component peaks in the core-level spectrum of N and Ag for the chitosan acetate - silver system. After charging correction.

Binding Energies (eV)						
Nitrogen (N)			Silver (Ag)			
			3d <sub>3/2</sub>		3d <sub>5/2</sub>	
400.8	402.0	403.2	375.6	376.5	369.6	370.4
400.2	401.3	403.3	375.5	376.6	369.5	370.6
399.0	402.6	402.6	375.0	375.9	369.0	370.1

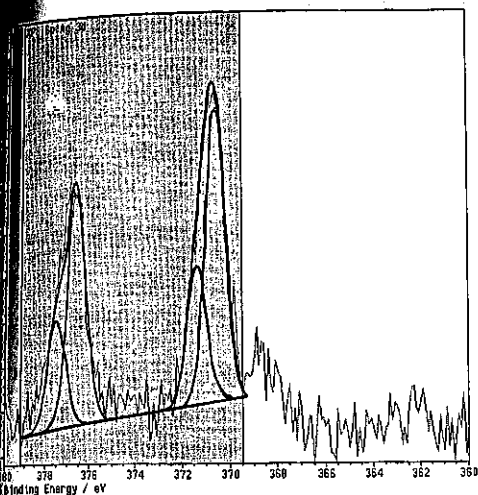


Figure 1. Narrow scan for Ag 3d signal obtained from sample containing 6.7 wt. % silver triflate. Not corrected for charging effect.

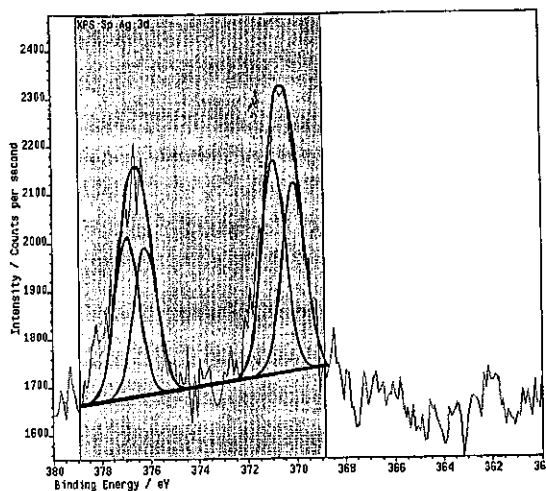


Figure 2. Narrow scan for Ag 3d signal obtained from sample containing 13.4 wt. % silver triflate. Not corrected for charging effect.

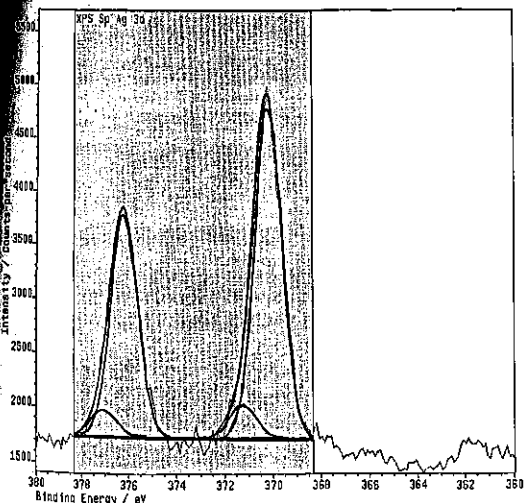


Figure 3. Narrow scan for Ag 3d signal obtained from sample containing 46.9 wt. % silver triflate. Not corrected for charging effect.

The different binding energies are referred to the XPS handbook. It has been reported that N 1s binding energy in NH<sub>3</sub> lies between 398.7 eV to 399.6 eV [2]. Hendrickson *et.al* [3] has reported N 1s binding energy in NH<sub>3</sub> at 399.6 eV and Larkins and Lubenfeld [4] at 398.7 eV. Our results seem to be in reasonable agreement with those reported. The binding energy in the second column is attributed to the chitosan-acetate salt. This is by virtue of the result given by Yoshida and Sawada [5] for the N 1s binding energy in H<sub>3</sub>N(CH<sub>2</sub>)<sub>3</sub>COOH at 400.8 eV which is closest to the result at 401.3 eV in the present investigation. The binding energy in the third column is therefore inferred to be the N 1s binding energy for the interaction between N of chitosan and the Ag<sup>+</sup> cation of the silver triflate salt. From the XPS handbook [2], the maximum binding energy for Ag 3d<sub>5/2</sub> electron in silver compound is 369 eV i.e. for AgOCCF<sub>3</sub>. The binding energy for Ag 3d<sub>5/2</sub> electron obtained in

the present investigation (369.0 to 369.6 eV) can be assigned to the Ag 3d<sub>5/2</sub> electron in silver triflate as shown in Figures 1 to 3. Likewise, the binding energy ranging from 375.0 to 375.6 eV is attributed to the binding energy of Ag 3d<sub>3/2</sub> electron of the silver salt. The gaussian component peaks at the higher binding energies are attributed to Ag-N interaction.

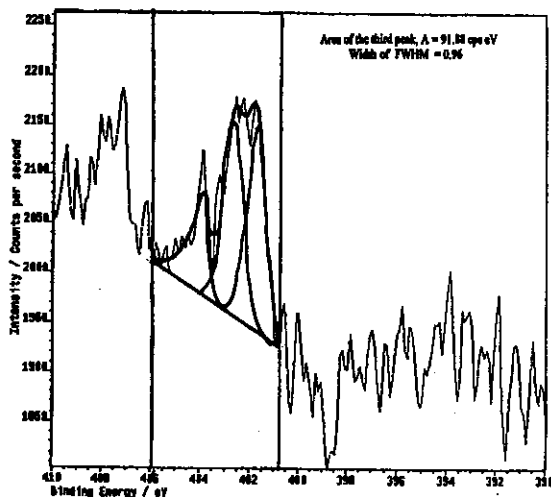


Figure 4. Narrow scan for N 1s signal obtained from sample containing 6.7 wt. % silver triflate. Not corrected for charging effect.

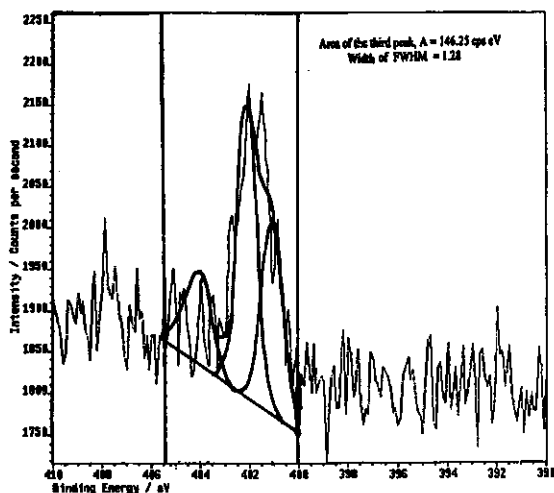


Figure 5. Narrow scan for N 1s signal obtained from sample containing 13.4 wt. % silver triflate. Not corrected for charging effect.

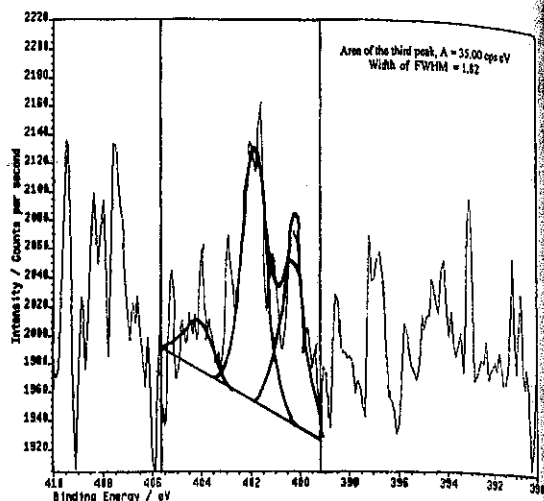


Figure 6. Narrow scan for N 1s signal obtained from sample containing 46.9 wt. % silver triflate. Not corrected for charging effect.

From the intensity of the gaussian component peak assigned to the Ag-N interaction it can be understood why the sample with 13.4 wt. % silver triflate added exhibits the highest electrical conductivity ( $10.20 \pm 0.08$ )  $\mu\text{S cm}^{-1}$  at room temperature. Since the peak at the higher binding energy is attributed to Ag-N interaction, the increase in intensity of such peak indicates more complexation has taken place. When these complexed sites vibrate about the equilibrium position, there may come an instance whereby the ion may attain sufficient energy to hop to another uncomplexed sites or hops to another complexed site and “knocks out” an Ag<sup>+</sup> ion which has to move to another vacant or occupied site. Thus charge is conducted within the material. The intensity of such gaussian peak in the sample with 13.4 wt. % silver triflate is higher than the intensity of the peak in the sample containing 6.7 wt. % and 46.9 wt. % silver triflate added. The sample with more complexation sites should exhibit the higher electrical conductivity. By virtue of this argument, the gaussian peak with the highest binding energy must present Ag-N interaction. The sample with 6.7 wt. % AgCF<sub>3</sub>SO<sub>3</sub> has a room temperature electrical conductivity of ( $8.86 \pm 0.09$ )  $\mu\text{S cm}^{-1}$  and that containing 46.9 wt. % AgCF<sub>3</sub>SO<sub>3</sub> has a room temperature electrical conductivity of ( $3.20 \pm 0.08$ )  $\mu\text{S cm}^{-1}$ . The decreases in electrical conductivity for the sample with high salt content could be due to ions association [6].

## CONCLUSION

It can be deduced that complexation occurs between the "soft"  $\text{Ag}^+$  cation and the secondary nitrogen atom in chitosan. The binding energy of the Ag  $3d_{3/2}$  electron in Ag-N interaction is between 375.9 to 376.6 eV and for the Ag  $3d_{5/2}$  electron is between 370.1 to 370.4 eV.

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