aysian Journal of Science 21A: 169-171 (2002)

$2p_{1/2}$ and Zn $2p_{3/2}$ electron binding energies with nitrogen in tosan-zinc acetate membranes determined by x- ray photoelectron ctroscopy studies

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TRACT Chitosan and zinc acetate complexes were prepared by dissolving the polymer in rent amount of salt and in 100 ml 1 % acetic acid solution and casting the solutions onto various petri s for film formation at room temperature. Complexation between the zinc cation and the nitrogen in the amine group of the chitosan can be proven by x-ray photoelectron spectroscopy (XPS). The at ~ 401 eV indicates N-Zn interaction. The peaks at ~ 1025 eV and ~ 1048 eV are attributable to the $p_{3/2}$ and Zn $2p_{1/2}$ electron binding energy with the nitrogen donor in chitosan.

osan, Zinc acetate, XPS, Gaussian component peak)

INTRODUCTION

is a powerful tool to characterize materials is particularly useful in proving the rrence of complexation between a salt and a ner. It can detect the photoelectron from the of an atom or element and the signal due to lectron is "recognizable" or distinguishable the core electron emitted from other ents due to the difference in their kinetic and ng energies. Such electronic signals can be er deconvoluted by sophisticated curve g techniques, which enable more mation about the sample to be obtained. The lexation occurs between the zinc cation of alt and the nitrogen atom of the amine group itosan. The nitrogen atom is able to form a with the cation of the salt since it has a pair nshared electrons [1]. As an example, a san-$LiCF_3SO_3$ (lithium triflate) film can be ed by dissolving chitosan and $LiCF_3SO_3$ in l etic acid solution and casting the solution l petri dish at room temperature to form the [2-3]. A small portion of the film can be prepared for XPS studies and a wide spectrum should show the presence of Zn, C, S, F, N and O signals. The Zn 2p and N 1s signals, for example, can be deconvoluted into several Gaussian component peaks. From these, the binding energies can be determined. It is the purpose of this work to determine the Zn 2p electron binding energy with the nitrogen donor atom in chitosan.

EXPERIMENTAL

The XPS studies in this work were carried out using a Kratos XSAMHS surface analysis spectrometer with an Mg K_α x-ray source (1523.6 eV), which is available at the School of Applied Physics, Faculty of Science and Technology, University Kebangsaan Malaysia. The spectrum was recorded at an operating current and voltage of 10 mA and 14 kV, respectively. The spectrometer was calibrated using a clean Ag plate and the Ag $3d_{5/2}$ line was set at 368.25 eV. The C 1s binding energy at 284.5 eV was used as a second reference. The

solid polymer sample was mounted onto a standard stub holder using double-sided adhesive tape. The survey scan was recorded in the energy range between 10 eV to 1100 eV. The pass energy and step size energy was 160 eV and 1 eV $step^{-1}$ respectively. Sweep time was set at 300 seconds per sweep. For the narrow scan, smaller pass energy of 20 eV with lower step size, 0.1 eV $step^{-1}$ was utilized. The sweep time was 59.898 seconds per sweep. Narrow scans were obtained for the C 1s, O 1s, N 1s, Zn $2p_{3/2}$, and Li 1s signals. The sample analysis chamber was kept at $\approx 5.0 \times 10^{-9}$ torr or less during the scans. The vision software provided by Kratos deconvoluted all core-level spectra into gaussian component peaks. Charging effects were corrected for using the C 1s binding energy at 284.5 eV. In this work, low molecular weight chitosan is used.

RESULTS AND DISCUSSION

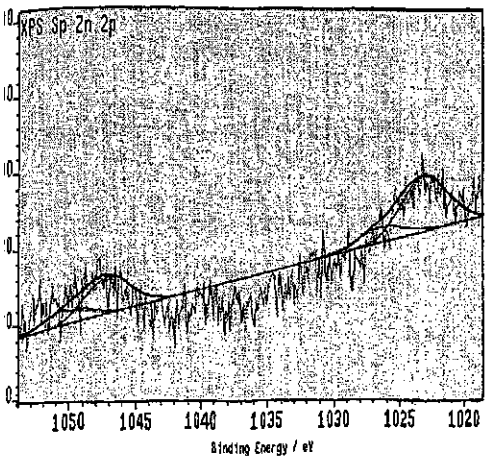
Table 1 lists the binding energies for the Zn and N interactions. The difference between the binding energies of the Zn $2p_{1/2}$ electron and that of Zn $2p_{3/2}$ electron is approximately the same with the difference in binding energies given in the handbook of XPS [4].

The peaks at 1020.7, 1021.8 and 1023.2 eV are attributable to the Zn $2p_{3/2}$ electron binding energies in zinc acetate. The reference value of this binding energy is 1021.4 eV [4]. Since the Zn $2p_{3/2}$ and Zn $2p_{1/2}$ width is 23 eV [4], the 1044 to 1046 eV binding energy is attributed to Zn $2p_{1/2}$ electron binding energy in zinc acetate. However, there is no reported data about the second gaussian component peak in the $2p_{3/2}$ and $2p_{1/2}$ envelopes.

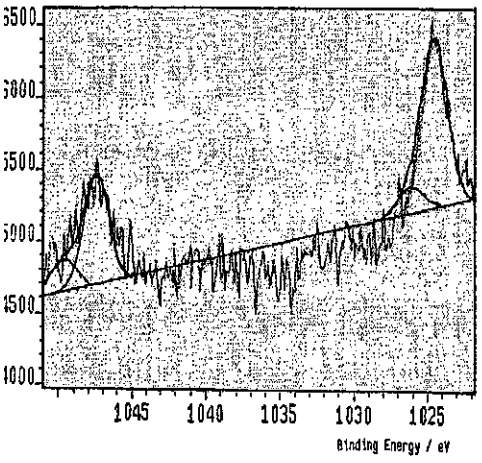
Muzzarelli [5] has reported that zinc chelates with chitosan. It can be observed that the intensity of zinc acetate peak in the sample containing 6.7 wt. % salt is higher than the intensity of the peak attributed to the Zn-N interaction. This is also true for the sample containing 26.8 wt. % zinc acetate. However in the sample containing 46.9 wt. % zinc acetate the peak attributable to zinc acetate has a lower intensity than its counterpart. This strengthens the motion that the second peak at the higher binding energy in the $2p_{3/2}$ and $2p_{1/2}$ envelopes is attributable to Zn-N interaction. If this is so then it can be inferred that there are more complexation sites and the conductivity of this sample is expected to be higher than that containing 6.7 wt. % and 46.9 wt. % salt. This is because when more zinc salt has complexed with the N atoms, the Zn ions can be transferred from one complexation site to another through some thermally assisted mechanisms. The conductivity of the sample containing 6.7 wt.% is 2.94×10^{-8} S cm^{-1}, that containing 26.8 wt. % is 4.42×10^{-8} S cm^{-1} and that containing 46.9 wt. % is 8.84×10^{-8} S cm^{-1}. Figures 1 to 3 depict the narrow scan of Zn $2p_{1/2}$ and Zn $2p_{3/2}$ signals obtained from samples containing 6.7 wt. %, 26.8 wt. % and 46.9 wt. % zinc acetate.

Table 1: Binding energies (eV) for N and Zn for samples containing 6.7 wt. %, 26.8 wt. % and 46.9 wt. % zinc acetate. Binding energy has been corrected for charging effect.

zinc acetate content	Binding energies (eV) Zinc (Zn)			
(wt. %)	$2p_{3/2}$		$2p_{1/2}$	
6.7	1021.8	1025.1	1045.8	1049.0
26.8	1023.2	1024.8	1046.1	1048.4
46.9	1020.7	1023.1	1044.9	1046.4



e 1. Narrow scan for Zn $2p_{1/2}$ and Zn $2p_{3/2}$ signals ıed from sample containing 6.7 wt. % zinc acetate. Not ıted for charging effect.



e 2. Narrow scan for Zn $2p_{1/2}$ and Zn $2p_{3/2}$ signals ed from sample containing 26.8 wt. % zinc acetate. ɔrrected for charging effect.

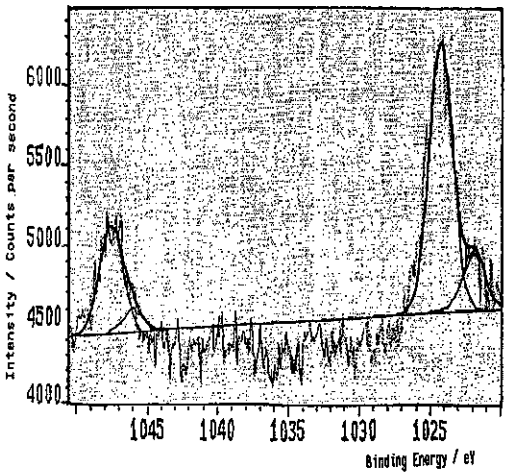


Figure 3. Narrow scan for Zn $2p_{1/2}$ and Zn $2p_{3/2}$ signals obtained from sample containing 46.9 wt. % zinc acetate. Not corrected for charging effect.

CONCLUSION

X-ray photoelectron spectroscopy (XPS) has confirmed the occurrence of complexation between polymer and salt. XPS has shown the possible binding energy due to Zn-N interaction at ~ 1025 eV (Zn $2p_{3/2}$) and ~ 1048 eV (Zn $2p_{1/2}$).

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