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Characterization of Silver-Binding Chitosan by Thermal Analysis and Electron Impact Mass Spectrometry

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ABSTRACT

Chitosan becomes thermally less stable as a result of complex formation with silver. A comparison of the thermal curves of a sample containing 210 mg silver g^{-1} chitosan with those of chitosan showed that not all the polymer is engaged in complex formation and only about 52% of the silver present is actually complexed, the remainder being retained by sorption. The evaporation curves obtained in mass spectrometry exhibited a maximum for chitosan and two maxima for silver-containing chitosan. A comparison of the peak ratios 80:60, 67:60 and 80:42 for the components of each maximum corroborates the fact that silver-containing chitosan can be considered as a mixture of complexed and uncomplexed polymer.

INTRODUCTION

Chitosan is the name given to a family of polymers obtained from extensive deacetylation of chitin (poly-*N*-acetyl-D-glucosamine) differing mainly in degree of deacetylation — generally ranging from 70 to 85% — and molecular weight as a result of the harsh chemical treatments involved. Therefore, several methods have been developed for the rapid characterization of chitosan, including the use of thermal analysis

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(García-Alonso *et al.*, 1983), infrared spectroscopy (Hirano *et al.*, 1976; Peniche-Covas *et al.*, 1984) and mass spectrometry (Scholtzhauer *et al.*, 1976; Mattai & Hayes, 1982) for the determination of the degree of deacetylation of chitosan.

Chitosan has a considerable capacity for metal-ion collection, mainly through ion exchange, sorption and chelation (Muzzarelli, 1977) and this ability has proved to be useful for many industrial purposes (Muzzarelli, 1977; 1983). The mechanism of metal-ion binding to chitosan has been studied by different techniques, including energy dispersive analysis of X-rays (EDAX) and electron spectroscopy for chemical analysis (ESCA) (Eiden *et al.*, 1980). In the present work use is made of thermal analysis and electron impact mass spectrometry to characterize silver-binding chitosan.

MATERIALS AND METHODS

Chitosan obtained from the shells of lobsters (*Panulirus argus*) in a pilot plant was dissolved in 0·2 M acetic acid and precipitated in 0·1 M sodium hydroxide. The solid was treated with 0·1 M EDTA solution in ammonia buffer (pH 10), washed with deionized water and dried. The ash content of the polymer thus obtained was below 0·15%. The percentage of amino groups was 6·5% as determined by potentiometric titration with 0·1 M NaOH of chitosan dissolved in 0·1 M HCl.

Silver-binding chitosan was prepared by stirring chitosan powder (200 mg) for 1 h in 0·1 M silver nitrate (20 ml) at 25°C and pH 6·5. The solid was separated by filtration, washed with deionized water and dried over phosphorous pentoxide. The amount of ionic silver retained by the polymer was 210 ± 10 mg silver g^{-1} chitosan as determined by analysis of both the solid and the $AgNO_3$ solution before and after the interaction by Volhard's method.

Thermal analysis was performed on a Labor MIM derivatograph model 1000 TIR, with the Paulik–Paulik–Erdey system (Labor MIM, Hungary). Curves were recorded on photo-sensitive paper using 60 mg of sample and a heating rate of 10°C min^{-1} in air.

Mass spectra of initial chitosan and the complex were recorded on a JEOL, DX-300 mass spectrometer (Japan) by direct sample introduction with a heating program for the probe from 80 to 400°C at 64°C min^{-1}. Experimental conditions were: source temperatures, 200 and 280°C; ionization voltage (EI), 70 eV; accelerating voltage, 3 kV; ionization current, 300 μA; multiplicating voltage, 150 V. Spectra were registered at one decay per second on hard-disks (4·56 megabytes) and processed on a Jeol mass data analysis system model JMA-3100.

RESULTS AND DISCUSSION

The Differential Thermal Analysis (DTA) curve of chitosan shown in Fig. 1 exhibits the typical behaviour reported for this polymer (García-Alonso *et al.*, 1983). A first endothermic effect is observed with a maximum decomposition rate at 60°C (Differential Thermogravimetric, DTG curve) associated with a weight loss of 13% (absorbed water), followed by two strong exothermic effects at 280 and 480°C; the first with maximum decomposition rates at 280 and 320°C, associated with weight losses from the non-acetylated and acetylated units, respectively, and the second with a maximum decomposition rate at 500°C, characteristic of the residual decomposition.

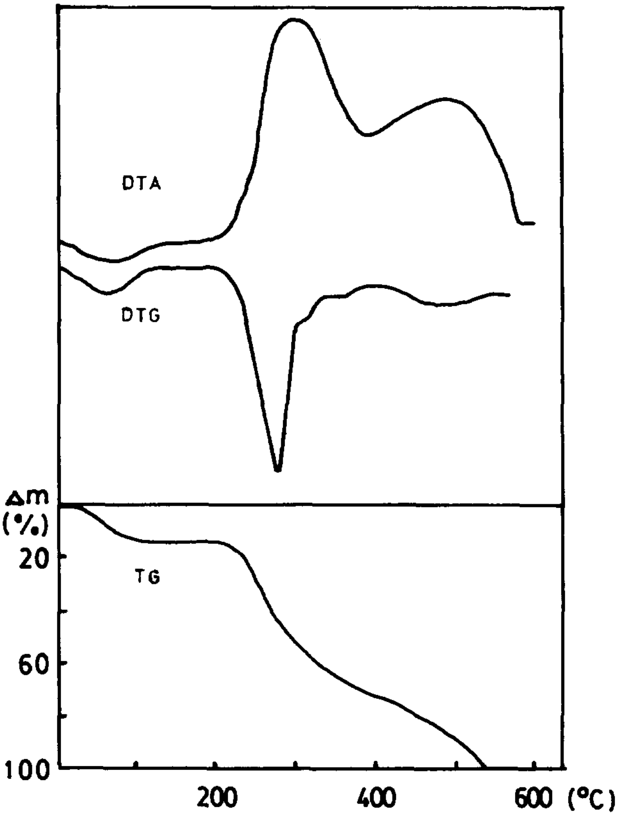

Fig. 1. DTG, TG and DTA curves for chitosan.

The DTA curves of the silver-containing chitosan (Fig. 2) showed an initial endothermic effect with a maximum decomposition rate at 80°C, associated with a weight loss of 12% (absorbed water) followed by three

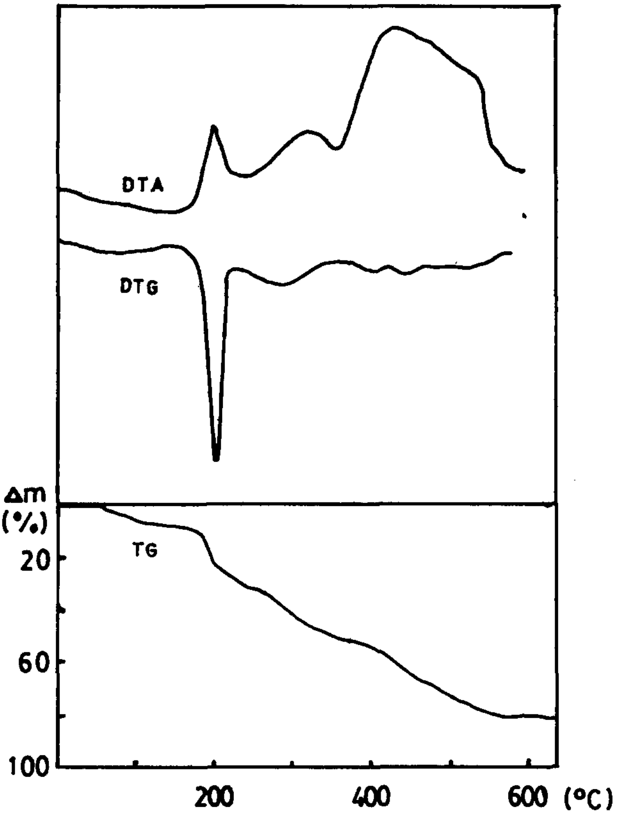

Fig. 2. DTG, TG and DTA curves for silver-containing chitosan.

exothermic effects — instead of the two observed for the starting chitosan — at 200, 320 and 400°C, with maximum decomposition temperatures at 200, 280 and 320 and 400, 440 and 500°C, respectively. Thermogravimetric (TG) curves showed that whereas chitosan left practically no residues after decomposition, silver-containing chitosan left 19% due to residual silver oxide. It was significant that the silver content calculated on this basis (218 mg g^{-1}) was consistent with that obtained by chemical analysis (210 mg g^{-1}). The percentage weight losses associated with the fundamental thermal effects are summarized in Table 1 for the starting chitosan as well as for silver-containing chitosan.

The shift to lower temperatures of chitosan's first exothermic effect observed for silver-containing chitosan is probably due to thermal unstabilization of the amino groups involved in complex formation as compared to free amino groups. The percentage weight loss of the complex at 280°C — which is due to the contribution of the non-acetylated form of chitosan — was only 48% of that observed for starting

TABLE 1
Percentage Weight Losses Associated with the Fundamental Thermal Effects (Calculated for Moisture- and Ash-free Samples)

DTG peak temperatures (°C)	*Chitosan*	*Silver-containing chitosan*
200	—	11·1
280	46·0	22·2
320	7·4	5·6
360	9·2	—
400	—	5·6
440	—	9·7
500	27·6	22·2

chitosan at the same temperature (see Table 1) indicating that 52% of the amino groups are involved in complex formation.

Silver-ion retention by chitosan is not only caused by complex formation but also by sorption. Nevertheless, on the basis of the above results the amount of silver ion actually involved in complex formation can easily be determined.

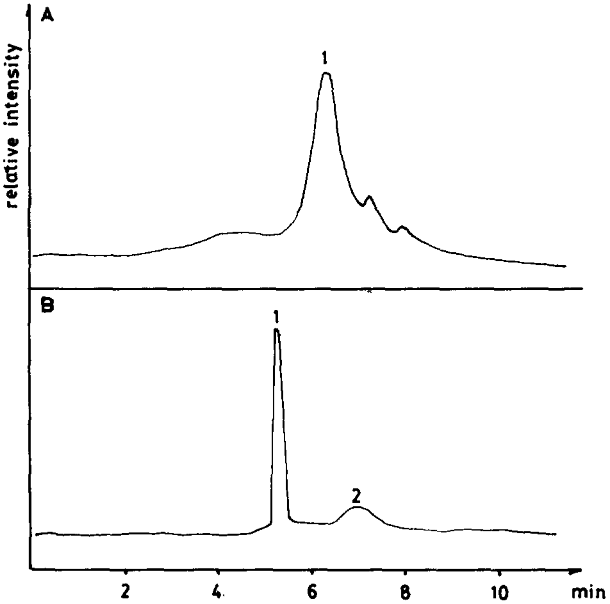

Fig. 3. Evaporation curves obtained by direct sample introduction electron impact mass spectrometry: (A) chitosan (peak 1); (B) chitosan (peak 1), chitosan–silver complex (peak 2).

The molecular weight of the average equivalent unit of chitosan is 246 calculated on the base of 6·5% of amino groups, so that 1 g of polymer contains $4{\cdot}1\times10^{-3}$ mole of amino groups, of which 52% ($2{\cdot}1\times10^{-3}$ mole) are complexed with $1{\cdot}05\times10^{-3}$ mole of silver — 52% of the total amount of metal ion retained — on the consideration that each silver ion is associated with two amino groups.

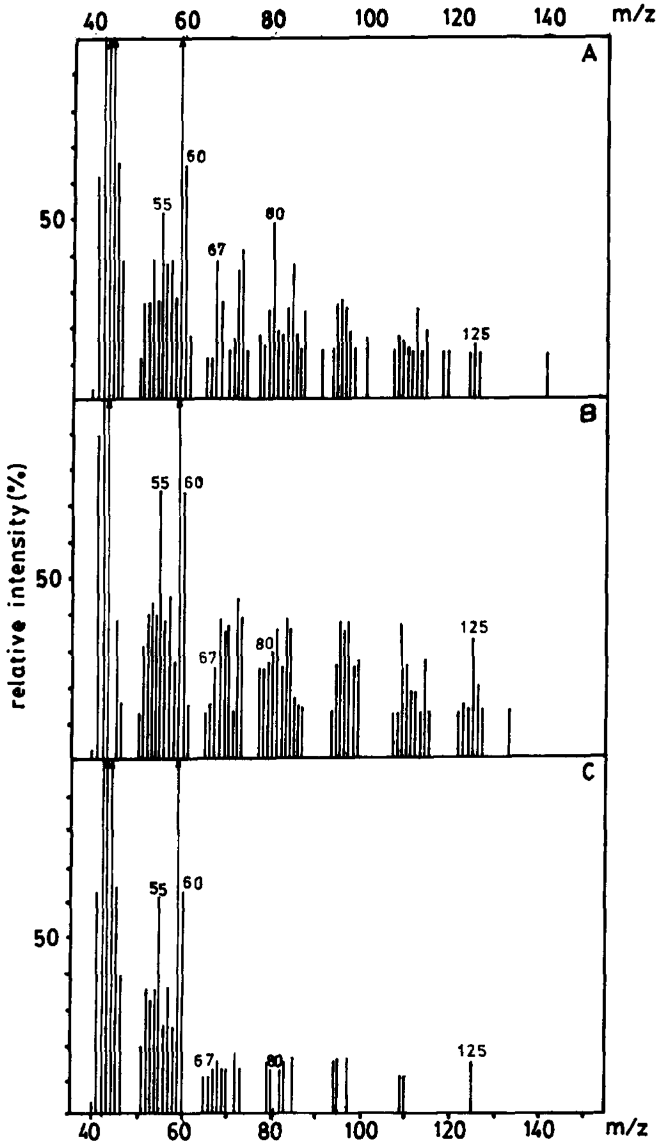

Fig. 4. Mass spectra of chitosan (A) and the components of the first (B) and second (C) peaks in Fig. 3B.

Figure 3 shows the evaporation curves obtained by mass spectrometry for starting chitosan (Fig. 3A) and silver-containing chitosan (Fig. 3B). The presence of two maxima in the curve of the latter indicates that it decomposes in a different way as compared with chitosan. The complex was thermally stable up to a temperature range between 186 and 202°C, and the analysis of the influence of the filament temperature in the ion source showed that best results are obtained at 280°C. When filament temperature was decreased down to 220°C, the relative intensities of various fragments of interest consequently diminished. Mass spectra obtained with a filament temperature of 280°C are shown in Fig. 4 for chitosan (Fig. 4A) and silver-containing chitosan (Fig. 4B and 4C) using the m/z ratio 42 as the base peak. Figure 4B corresponds to the mass spectrum of the component of the first peak in Fig. 3B, and Fig. 4C corresponds to the second peak.

The chitosan spectrum was identical to that reported by Mattai & Hayes (1982). They observed that peaks at m/z 67 and 80 were of high intensity in the chitosan spectrum and were of low intensity for chitin and *N*-acetyl-D-glucosamine, indicating that these fragments originated in the D-glucosamine moiety of the polymer, while those at 60 and 42 were from the *N*-acetyl-D-glucosamine moiety, and using high resolution techniques they assigned the corresponding fragments to each of the four peaks. They showed that the peak ratios 80:60, 67:60 and 80:42 were very sensitive to the amine content of the polymer, increasing as the degree of deacetylation increased.

Table 2 shows the peak ratios 80:60, 67:60 and 80:42 calculated for starting chitosan and both components of silver-containing chitosan. It can be concluded from these experimental data that the component of

TABLE 2

Peak Ratios for Chitosan and the Two Components of Silver-containing Chitosan Obtained by Electron Impact Mass Spectrometry

m/z ratio	*Peak ratios*		
	Chitosan	*Silver-containing chitosan*	
		Peak 1[a]	*Peak 2*[a]
80:60	0·47	0·50	0·20
67:60	0·58	0·43	0·20
80:42	0·36	0·33	0·13

[a] Peaks shown in Fig. 3B.

the first peak in Fig. 3B originates essentially in that part of chitosan remaining unaltered after the interaction with silver nitrate, while the component of the second peak (Fig. 3B) exhibited a considerable decrease in the peak ratios considered, undoubtedly caused by complexation of the silver ions with the amino groups of the D-glucosamine moieties of the polymer.

Both techniques, differential thermal analysis and mass spectrometry, were concordant in the characterization of silver-containing chitosan and proved to be very useful in studying the nature of the interactions of chitosan with metal ions.

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