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CHARACTERIZATION OF CHITOSAN BY PYROLYSIS–MASS SPECTROMETRY, THERMAL ANALYSIS AND DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

The thermal behaviour of chitosans with various degrees of deacetylation has been studied. The differential scanning calorimetry curves of the samples exhibit two peaks. The first, due to the loss of reticular water, is endothermic, with a peak temperature of 100 °C, whereas the second is exothermic, with a maximum at 310 °C, and is associated mainly with the first decomposition stage of the polysaccharide. It was found that the amount of energy liberated at this temperature increases as the deacetylation degree increases. Pyrolysis–mass spectra of chitosan samples with different degrees of deacetylation indicated that the peak (m/z) ratios 94:125, 80:125 and 80:110 increase as the degree of deacetylation increases, so that they may be used in the characterization of these polysaccharides in addition to the peak ratios 80:60, 67:60 and 80:42 already proposed.

INTRODUCTION

Chitosan is a polysaccharide very rarely found in nature, and is generally obtained by extensive deacetylation of chitin (poly-*N*-acetyl-D-glucosamine) in strongly alkaline media. It is difficult to achieve complete deacetylation of chitin, and what is usually known as chitosan is a family of products with a degree of deacetylation generally around 70 to 80%, and whose molecular weights vary not only with the starting raw material, but also with the specific conditions used for their preparation. This problem has motivated the development of a variety of techniques for characterization of chitosan [1].

Thermal degradation of chitin, particularly under pyrolysis conditions, can be of great value in the development of characterization techniques for these polymers. Thus, by thermal analysis of chitosans with different deacetylation degrees, it has been established that the thermal effect at 310 °C in

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the DTA curve of chitin strongly depends on the deacetylation degree of the polymer, and an empirical method has been developed for determination of the percentage of acetyl groups on the basis of thermogravimetric analysis. This method compared satisfactorily with one based on IR spectroscopy [2].

On the other hand, the characterization of chitosan by pyrolysis–mass spectrometry allowed correlation of the deacetylation degree, as amine group content, with the peak ratios 80 : 60, 67 : 60 and 80 : 42 [3].

Nevertheless, up to the present time little has been said about the degradation mechanism of these polysaccharides. In this work, use is made of thermal analysis, differential scanning calorimetry (DSC) and pyrolysis–mass spectrometry in order to obtain additional information on the degradation mechanism of chitin and chitosan.

EXPERIMENTAL

Samples of chitosan with different degrees of deacetylation and molecular weights were obtained from shells of lobsters (*Panulirus argus*) according to an established procedure [4]. The deacetylation degree was determined by Lee's method, as reported by Rutherford and Austin [5], and the molecular weights were determined by viscometry using Lee's solvent mixture for chitosan [6].

DSC curves were recorded in a Mettler calorimeter with a TA 4000 system using low temperature cells. The sample size was 10 mg and the heating rate was 5 °C min^{-1}.

Pyrolysis–mass spectra were registered in a JEOL HX-110 (Japan) mass spectrometer with a heating program from 30–400 °C. Experimental conditions were: ionization electron energy, 70 eV; accelerating voltage, 10 kV; ionization current, 300 μA.

RESULTS AND DISCUSSION

Figure 1 shows the thermogravimetric (TG) and differential thermogravimetric (DTG) curves of a chitosan sample with a degree of deacetylation of 85% (3% of acetyl groups) which exhibits the typical behaviour reported for this polysaccharide. The first peak in the DTG curve, with maximum decomposition rate at 53 °C, is associated with weight loss of 9.3% due to the release of water. The second peak, with maximum decomposition rate at 270 °C and a weight loss of 45.5%, is associated with the release of material from the non-acetylated and the acetylated units of the polymer [7].

The DSC curve in Fig. 1 exhibits two peaks corresponding to the fundamental thermal effects found in the DTG curve. The first is endothermic, with a peak temperature at 100 °C, and the second is exothermic, with

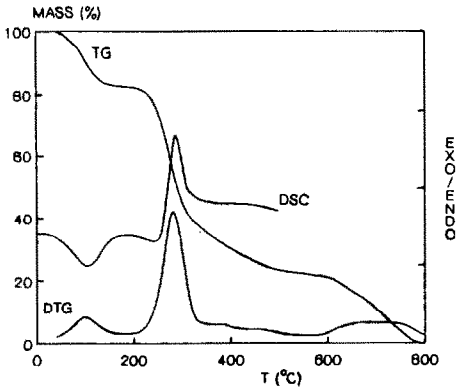


Fig. 1. Thermal analysis of chitosan in air (Sample B in Table 1).

a maximum at 310 °C. The energy absorbed during the first process amounts to 111 J g^{-1}, which is almost ten times the energy required to vaporize all the liberated water, indicating its reticular nature. This is in agreement with the findings of Nishi et al. [8], who by means of elemental analysis determined that chitin is strongly attached to 0.5 mol of water for each *N*-acetylglucosamine residue.

DTA curves reported for chitosan [2] exhibit two characteristic exothermic effects at 280 and 460 °C, the second one corresponding to the residual decomposition. It is evident that the exothermic effect found in the DSC curve (Fig. 1) is associated mainly with the first decomposition stage of the polymer. Table 1 shows that the amount of energy associated with this effect is strongly dependent on the deacetylation degree, and apparently independent of the molecular weight.

In fact, as can be seen from the table, as the deacetylation degree of the sample increases, the amount of energy liberated increases, indicating that the decomposition of the acetylated units is an endothermic process. The decrease in the crystallinity of chitosan with increase in the degree of deacetylation [9] will also contribute to modify the amount of energy evolved in the same direction, but could not do so substantially owing to the low degree of crystallinity of these samples.

TABLE 1

Energy liberated at 310 °C by chitosans with different degrees of deacetylation

Chitosan	CH_3CO (%)	$\overline{M}_v \times 10^{-4}$	ΔH_{sp} (J g^{-1})
A	6.0	3.93	−193
B	3.0	12.0	−220
C	0.8	1.17	−289

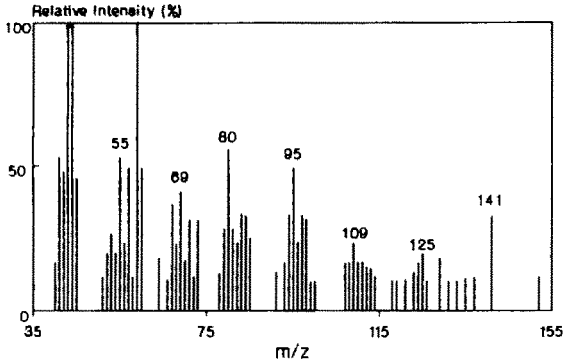
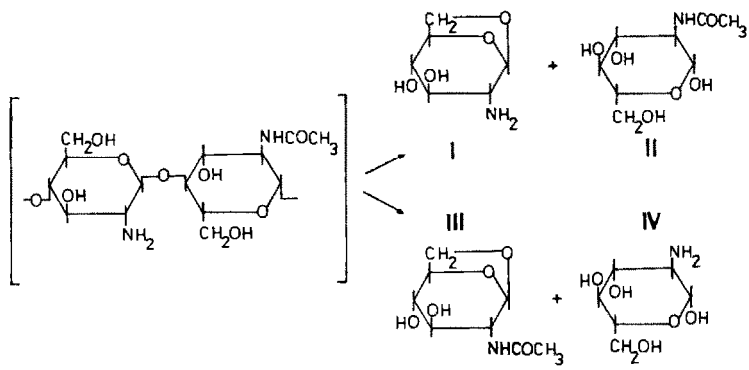


Fig. 2. Mass spectrum of chitosan (Sample B in Table 1).

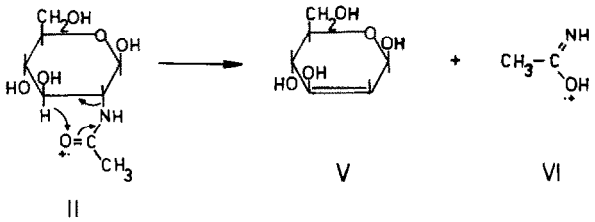
Figure 2 shows the mass spectrum of sample B (Table 1), which does not differ essentially from the spectra previously reported [3,7]. In this case the base peak corresponding to $m/z = 59$ has been taken as reference. Peaks with relative intensities smaller than 10% of the reference peak were eliminated, as well as peaks with m/z below 40.

Hayes and Davies [11] postulated that the fragments observed in the mass spectra of chitosan are derived from the acetylated and deacetylated units produced by rupture of the β-glycosidic linkages between the glucosamine and *N*-acetylglucosamine moieties. Thus, in spite of the significant difference existing between the derivatograms of chitin and cellulose [12], it is to be expected that at least the thermal scission of the intercatenary bonds in chitin and chitosan will lead, as in cellulose, to the formation of hydroxyl and levoglucosan terminals [13], giving rise to the structures shown in Scheme 1.

Structures II and III, having a carbonyl group and a hydrogen atom in the γ position, are susceptible to undergoing a rearrangement of the McLafferty type, as depicted in Scheme 2.



Scheme 1.



II V VI

Scheme 2.

On this basis, a contribution of fragment V to the peak at m/z 59 present in the mass spectra of this family of homologous compounds is to be expected. In fact, the most abundant fragment of the peak at m/z 59 has been identified as acetamide, and it has been shown that the intensity of this peak is less pronounced in the mass spectrum of chitosan [14].

Mattai and Hayes [3] have shown that the peak ratios 80 : 60, 67 : 60 and 80 : 42 increase as the deacetylation degree increases. This is due to the fact that the peaks at $m/z = 80$ (from the fragment C_5H_6N) and 67 (from fragments C_4H_5N and C_5H_7) were of lower intensity in chitin and in *N*-acetyl-D-glucosamine, indicating that they originated from the D-glucosamine unit of the polymer, while those at $m/z = 60$ ($C_2H_4O_2$) and $m/z = 42$ (C_2H_2O and C_2H_4N) came from the *N*-acetyl-D-glucosamine unit. The assignment of these fragments was carried out by these authors by means of high resolution techniques.

The existence of a functional relationship of this kind does not exclude the possibility of fragmentation of the acetylated units in an analogous way to the deacetylated units, only in this case fragments with higher m/z ratios are to be favoured, mainly due to the mass increment produced by the acetyl

TABLE 2

Peak ratios for chitin and chitosan

m/z ratio	Peak ratios			
	Chitin [a]	Chitosans (amino groups per cent indicated)		
		6.5 [b]	7.12 [c]	8.04 [a]
80: 60	0.26	0.47	1.1	1.5
67: 60	0.25	0.58	0.75	1.0
80: 42	0.17	0.36	1.1	1.0
80:110	1.1	2.5	3.3	7.0
80:125	0.9	2.1	2.8	10.5
94:125	0.52	1.7	2.5	9.7

[a] Taken or calculated from [3].
[b] Taken from [7].
[c] Sample B in Table 1.

groups present in the decomposing units. In fact, even though peaks with m/z values of 94, 110 and 125 do appear in the spectrum of chitosan, their relative intensity is smaller when compared with chitin and *N*-acetyl-D-glucosamine.

In Table 2 the peak ratios 80:110, 80:125 and 94:125 are shown, together with the peak ratios 80:60, 67:60 and 80:42. These peak ratios were calculated for chitin and for three samples of chitosan with different degrees of deacetylation. It can be seen that the peak ratios 94:125, 80:125 and 80:110 are as sensitive to the degree of deacetylation as the peak ratios previously reported, and can also be used as an indication of the percentage of amino groups in these polysaccharides.

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