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Thermogravimetric studies of chitosan derivatives

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Abstract

The thermal stabilities of chitosan derivatives (chito; 2-amino-2-deoxy(1-4)-β-D-glucopyranan) have been studied by thermogravimetry (TG) between 25 and 550 °C under nitrogen flow. The kinetic data thus obtained indicate that the thermostabilities decrease in the order, chito-salicylaldehyde > chito-thioglycolic acid > chito > chito-butanoyl chloride > chito-4-Br-aniline > chito-4-NO_2benzene > chito-benzoic acid > chito-benzoyl chloride. The thermal stability apparently depends on the kind of bond established between the chitosan and the reactants. Schiff bases are more stable than amides and alkyl amines. The order of reaction for the thermal decomposition of these chitosan polymers ranges between −0.5 and −1.0. This is probably due to several overlapped processes. The pre-exponential factor, the reaction order and the activation energy of the decomposition for chitosan derivatives have been determined.

1. INTRODUCTION

Chitosan is a high molecular mass polysaccharide, insoluble in a neutral or alkaline aqueous solvent but soluble in dilute organic acids [1], and is thus a unique polymer with great potential application. Chitosan has been used for coagulation of protein, detection of ions, and in recovery of heavy metals [2,3]. This study describes the thermal stability of this polymer and its derivatives.

By considering the thermal behaviour of polymers as a function of the mass loss and the temperature of the system, it is possible to obtain information about their stability. Thermogravimetry (TG) has been used as a method of investigation of the thermal stability and characteristics of thermal decomposition of polymers. Kinetic parameters such as activation energy, pre-exponential factor and reaction order, give a quantitative measure of thermal stability [4]. Since there have been no reports related to

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chitosan and chitosan derivatives, we have developed thermal degradation studies. We report here several chitosan derivatives prepared with salicylaldehyde, thioglycolic acid, butanoyl chloride, 4-bromoaniline, 4-nitrobenzene, benzoic acid and benzoyl chloride.

EXPERIMENTAL

Synthesis of chitosan and its derivatives

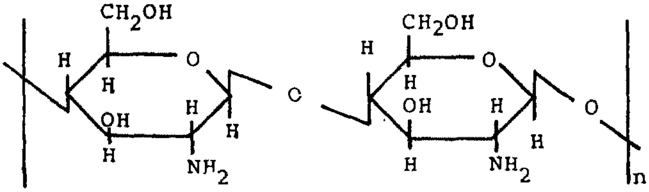
The synthesis of chitosan and its derivatives has been reported elsewhere [5].

Thermogravimetry

Thermogravimetric data were obtained using a Perkin Elmer TGS-1 thermobalance with a Perkin Elmer UU-1 temperature program control. Samples (1–5 mg) were placed in aluminium pans and heated under flowing nitrogen (50 ml min^{-1}) at a rate of 10 °C min^{-1} between 298 and 823 K.

RESULTS AND DISCUSSION

The synthesis of chitosan has already been reported [6]. We prepared chitosan using a modification of the Fujita method and as starting material, three types of crab from the Talcahuano area of Chile.



Chitosan.

Chitosan has been tested as seed treatment and for foliar applications to field crops. Some of the seed treatment applications resulted in cost effective increases in yield [7].

The viscosimetric molecular weight range is between 0.5×10^5 and 1×10^5.

In Fig. 1 we can observe the change in sample mass as a function of time and temperature when the eight compounds are heated from 298 to 823 K. Table 1 shows the thermal decomposition temperature (T_D) for each polymer. These values were taken from the first large change in the slope of the TG curve.

The polymers degrade mainly in one stage and present a T_D around 500 K. The data suggest that the thermal stability of the polymers is influenced

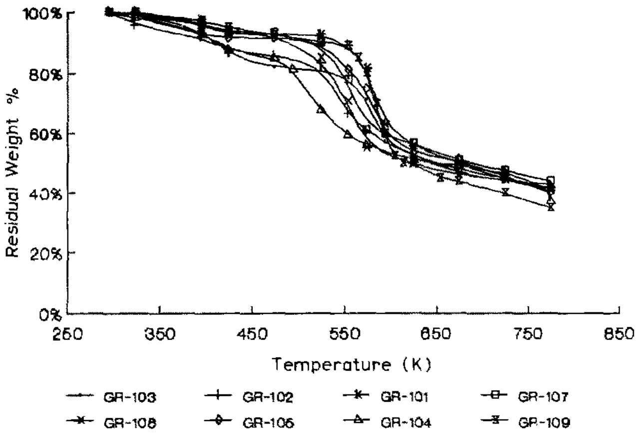


Fig. 1. Thermogravimetric curves of chitosan derivatives at a heating rate of 10 °C min^{-1}. |, Chitosan-1; ●, Chitosan-2; △, Chitosan-3; ◇, Chitosan-4; ×, Chitosan-5; □, Chitosan-6; X Chitosan-7. For abbreviations see footnote to Table 1.

by the kind of bond between the chitosan and the adducts. It is interesting to observe that chito-salicylaldehyde and chito-benzoic acid present the highest T_D values (553 and 540 K) and one of them exhibits the highest E_a value (C=N bond).

The most unstable polymer is the chito-NO_2-benzene (*N*-aryl amine) with a T_D of 483 K and a low E_a. Another unstable derivative is chito-benzoyl chloride (aryl amide) with a T_D of 493 K and the lowest E_a (41.88 kJ mol^{-1}).

The decomposition reaction is irreversible so that the rate dependent parameters such as activation energy and order of reaction may be calcu-

TABLE 1

Kinetic parameters for chitosan derivatives

Polymer [a]	Z (s^{-1})	E_a (kJ mol^{-1})	n	T_D (K)
Chitosan	3.2×10^2	70.92	−0.5	533
Chitosan-1	1.6×10^1	49.54	−1.0	483
Chitosan-2	3.8	45.77	−0.5	540
Chitosan-3	4.0	41.08	−0.5	493
Chitosan-4	4.8×10^2	69.33	−0.5	508
Chitosan-5	6.1×10^3	76.15	−1.0	498
Chitosan-6	8.8×10^2	69.33	−1.0	523
Chitosan-7	6.8×10^{11}	170.04	−1.0	553

[a] Chitosan-1, chito-4-nitrobenzene; chitosan-2, chito-benzoic acid; chitosan-3, chito-benzoyl chloride; chitosan-4, chito-4-Br-aniline; chitosan-5, chito-thioglycolic acid; chitosan-6, chito-butanoyl chloride; chitosan-7, chito-salicylaldehyde.

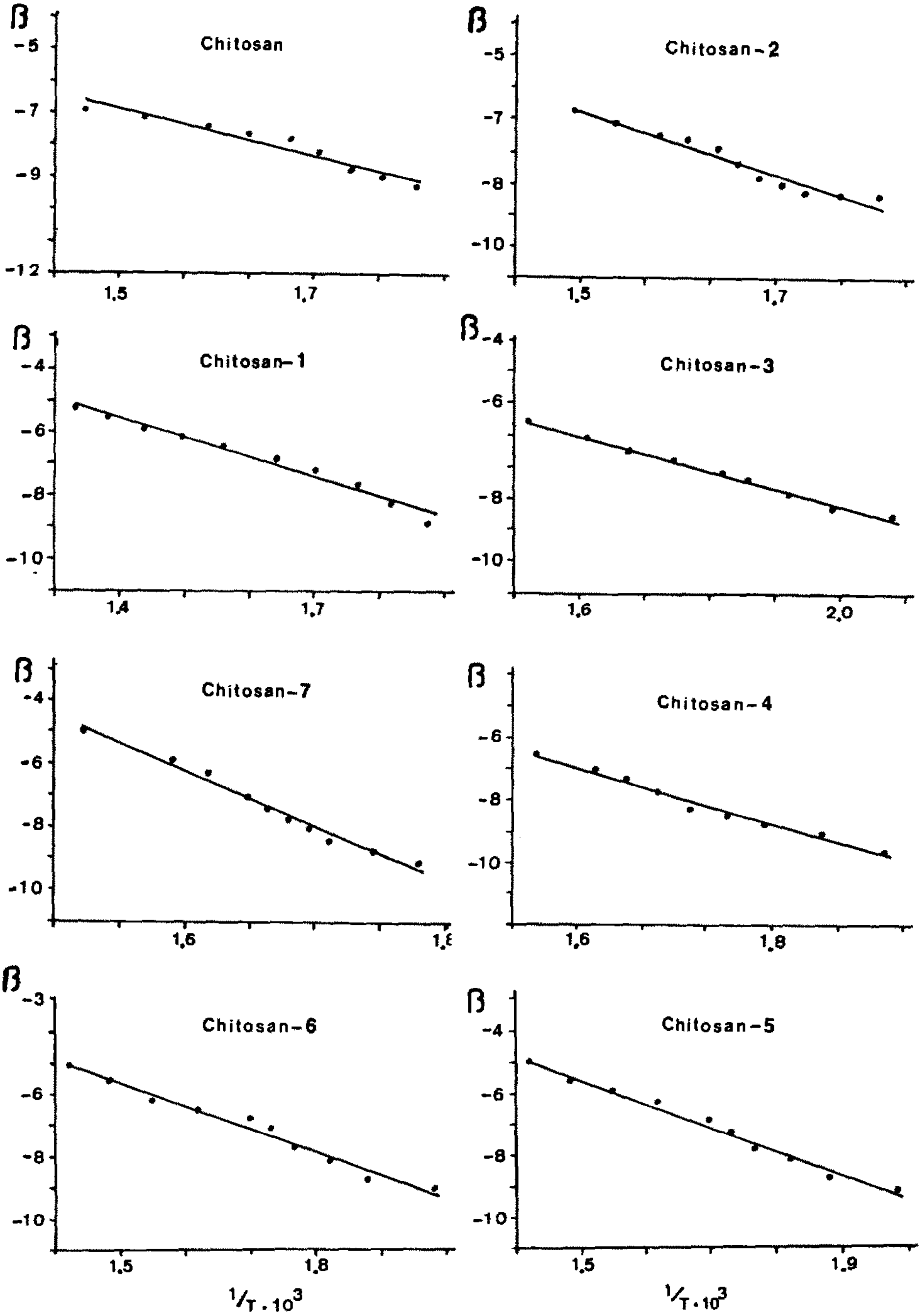


Fig. 2. Arrhenius plot for the thermal decomposition of chitosan derivatives according to eqn. (3).

lated from a single experimental curve [8]. The specific rate constant (k) can be expressed in the Arrhenius form

$$k = Z \exp(-E/RT) \tag{1}$$

where Z is the frequency factor, E the activation energy, R the gas constant and T the absolute temperature.

The thermal decomposition kinetics of the thermogravimetric mass loss were attributed to the equation

$$-\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(1-\alpha)^n \tag{2}$$

where α is a fraction of the sample mass reacted at time t, n is the reaction order and k is the specific rate constant. The reaction rate $\mathrm{d}\sigma/\mathrm{d}t$ was calculated using a differential technique and incorporating the heating rate, v, (10 ° C min^{-1}), using the data from temperature versus sample mass fraction [9]. After combining eqns. (1) and (2), incorporating v and using the logarithmic form

$$\beta = \ln\left[\frac{\mathrm{d}\alpha/\mathrm{d}t}{v(1-\alpha)^n}\right] = \ln A - \frac{E}{RT} \tag{3}$$

To calculate the kinetic parameters E and Z and assuming a first-order reaction model, a multiple regression program was used [10]. Plotting β versus $1/T$ should give a straight line (see Fig. 2). From the slope and intercept E and Z can be determined.

For chitosan-1, -5, -6 and -7 the linear relationship obtained indicated that the order of the reaction is -1. For chitosan and chitosan-2, -3 and -4 the order of the reaction is -0.5. This is probably due to a very complex decomposition mechanism for these polysaccharides. The coefficients of linear correlation vary from 0.967 to 0.996. The kinetic parameters E and Z calculated from these plots are summarized in Table 1.

In general, all the chitosan derivatives showed low activation energies, the only exception being chito-salicylaldehyde (170.04 kJ mol^{-1} corresponding to the C=N bond). All the other derivatives are within the same range of metal poly(methyl methacrylates) already reported [11]. These values range from 41.88 kJ mol^{-1} to 76.15 kJ mol^{-1} for chito-benzoyl chloride and chito-thioglycolic acid, respectively.

The kinetic parameters obtained for the thermal decomposition of these polymers showed a relationship between the type of bonding present in each derivative. Amides and aryl amines are the most stable compared with alkyl amines. The only relevant compound is the Schiff base which seems to be very stable showing the highest E_a and T_D.

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