Kinetics and mechanism of the thermal degradation of biopolymers chitin and chitosan using thermogravimetric analysis

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ABSTRACT

In this work, the kinetics of thermal degradation of chitin and chitosan polymers were investigated by means of Fourier Transform Infrared Spectroscopy and thermogravimetric analyses in air atmosphere, under dynamic conditions in the range of 298–873 K. The kinetic parameters, such as the apparent activation energy (E_a) and pre-exponential factor (A) were determined using Ozawa–Flynn–Wall (OFW) and Kissinger–Akahira–Sunose (KAS) isoconversional methods. The experimental data were found, in the range of conversion fraction $0.1 < \alpha < 0.8$, to be well described by the modified catalytic Sestak–Berggren (SB) model adapting the conversion function, $f(\alpha) = c\alpha^m(1-\alpha)^n$ with the adjusted values of m, n and c. It was found that the simulated curves issued from the model best fit those issued from the experimental data, indicating the same scission mechanism for the degradation of chitin and chitosan. It was found that the average value of $E_a = 125$ kJ/mol used in the simulated curves of chitin, $Y(\alpha)$ and $Z(\alpha)$, is comparable to those calculated by KAS and OFW, while for chitosan, it represents the mean value ($E_a = 169$ kJ/mol) between the values of E_a calculated by KAS ($E_a = 191.61$ kJ/mol) and OFW ($E_a = 146.50$ kJ/mol) methods.

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1. Introduction

Chitin is one of the most abundant natural amino-polysaccharide biopolymers found particularly in the shells of crustaceans, such as shrimp and crab and in the product of the fishing industry [1–3]. The chemical structure of chitin is a β-(1,4-)-linked polymer of 2-acetamido 2-deoxy D-glucopyranose (N-acetyl-D-glucosamine) [4]. The main derivative of chitin is chitosan which is obtained by N-deacetylation of chitin in hot alkaline medium with different deacetylation degrees (DD) [5,6]. Unique properties of chitin and chitosan make these biopolymers applicable in many fields due to: 1) high hydrophilicity given the great number of hydroxyl groups they possess; 2) a large number of chemically active amino groups and 3) a flexible structure of polymer chains that makes them compatible with the adsorption of metal ions.

In regards to the large fields of applications of these biopolymers, the accurate knowledge of their thermal degradation appears to be of great importance in order to define the

applications of such materials. Thermal behavior can be achieved by using some physical-chemistry techniques, especially thermal analysis methods DSC (differential scanning calorimetry), TGA (thermogravimetric analysis), DTG (differential thermal analysis), DMA (dynamic mechanical analysis), etc. Thermogravimetric analysis (TGA/DTA) has been widely used by many authors to investigate the kinetics of the thermal degradation in isothermal and dynamic conditions both in air and in nitrogen atmosphere. In most cases, the data can be applied to determine the degradation mechanism and the evaluation of kinetics triplet (E_a: activation energy, A: pre-exponential factor, $f(\alpha)$ conversion function) for commercial chitin and chitosan. For example, the data issued from the dynamic experiments by heating chitosan in N_2 atmosphere were treated by the methods proposed by OFW and KAS [7], resulting in apparent activation energy of 149.6 kJ/mol and 138.5 kJ/mol, respectively. While the approach proposed by Mac Callum was used to treat the data issued from the isothermal experiments, resulting in $E_a = 153$ kJ/mol. Cárdenas et al. [8] reported $E_a = 71$ kJ/mol by applying dynamic conditions for studying the thermal degradation of chitosan; and Peniche-Covas et al. [9] conducted their study in dynamic and isothermal conditions and found, respectively, $E_a = 181$ kJ/mol and $E_a = 183–227$ kJ/mol. Both studies were conducted in nitrogen atmosphere. In the case of chitin,

Georgieva et al. [10], determined an average value of Ea = 114.8 kJ/mol for activation energy for the second stage of the thermal degradation. T. Wanjun et al. found that the E_a values of chitin are almost constant (200–220 kJ/mol) with the conversion fraction α in the range of $0 < \alpha < 1$, while the E_a values of chitosan increase from 170 to 270 kJ/mol. Taking into account the articles published in this field, different values of the kinetic parameters Ea and A are obtained for commercial chitin and chitosan under the experimental conditions in which test they were performed (air or N_2). This is due to several causes, especially the origin of the studied polymers and the nature of side groups. As regards, the thermal degradation mechanism of these polymers, it is not clearly established. In most cases, the proposed kinetic models are based on ideal kinetic functions f(α), commonly used in the kinetic analysis of solid state decomposition, because it is demonstrated that these models can often describe the thermal degradation of polymers better than "n" order laws [11–13]. Recently, Sanchez-Jimenez et al. [14] developed a new kinetic model for random scission, which is the modified autocatalytic Sestak-Berggren model. In the literature, there are few reports which indicate that the degradation mechanism of chitosan follows the catalytic Sestak-Berggren model and the mechanism involving nucleation and growth, using Avrami–Erofeev function (A4) [15]. While in the case of chitin, there is no information about its thermal degradation mechanism.

The aim of this work is to get the kinetic parameters (E_a, A and f(α)) for the thermal degradation of chitin and chitosan, using thermogravimetric data, obtained in dynamic conditions. The results were compared with those obtained using commercial samples by applying different conventional calculating methods. The probable thermal degradation mechanisms of chitosan and chitin are discussed in relation with IR characterisation of these polymers at different temperatures. The thermal and kinetic data presented in this study should clarify the mechanism of degradation of both natural polymers (chitin and chitosan), obtained from the local shrimp shells.

2. Experimental

2.1. Materials and methods

As mentioned above, the natural chitin used in this work was extracted from shrimp shells collected from the fishmongers in the city of Meknes in Morocco, its deacetylation was made with a concentrated NaOH solution (12 N) for 6 h. The degree of deacetylation (DD) for chitin and chitosan is 14% and 82.5%, respectively. The reaction of deacetylation involves the removal of acetyl groups from the molecular chain of chitin and their replacement by the amino group NH_2, in the course of the reaction, to produce the chitosan (Fig. 1). Details of extraction reaction of chitin and its deacetylation as well as the determination of DD by using FTIR spectroscopy were published in our previous work [16]. HCl and NaOH were obtained from Aldrich Chemicals. All reagents were prepared in de-ionized water.

- **XRD**: The X-ray diffraction (XRD) patterns were obtained using an X'PERT MPD-PRO wide angle X-ray powder diffractometer provided with a diffracted beam monochromator and Ni filtered CuKα radiation (λ = 1.5406 Å). The voltage was 45 kV and the intensity 40 mA. The 2θ angle was scanned between $4°$ and $30°$, and the counting time was 2.0 s at each angle step (0.02°).
- **TGA/DTGA:** The dynamic degradation studies for the samples were carried out in air atmosphere in a TA60 SHIMADZU thermal analyser simultaneous TGA/DTA. The samples were heated from ambient to 873 K at the desired heating rate β (5, 10, 15, 20 K/min). The loss of weight was monitored, allowing the calculation of the extension of conversion as a function of the reaction time. The DTG curves were used to determine the rates of degradation of chitin and chitosan versus the extent of conversion α. The measuring accuracy of sample temperature was checked by the onset fusion temperatures of indium (T = 429.6 ± 1 K).
- **FTIR:** The structural changes, which took place during the degradation of the samples studied, were collected in the Fourier Transform Infrared Spectrometer (FTIR) (Shimadzu, JASCO 4100). The samples were prepared in KBr discs in the usual way from very well dried mixtures of about 4% (w/w). FTIR spectra were recorded by accumulation of at least 64 scans with a resolution of 4 cm^{-1} per sample.

2.2. Kinetic analysis

Various methods of kinetic analysis were used to determine the rate of reaction and the kinetic triplet for the thermal degradation reaction of a solid-state polymer. In thermogravimetric measurements, the rate of degradation reaction can be described by the following general equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

Where t is the time, T is the temperature, and $\alpha = \frac{m_0 - m_t}{m_0 - m_f}$ is the conversion fraction, determined as a ratio of the current mass change, $\Delta m = m_0 - m_t$, to the total mass change, occurred throughout the process with m_t, m_0 and m_f, respectively, are the actual, initial and final masses, $f(\alpha)$ is the conversion function which depends on the reaction model, and $k(T)$ is the rate constant. The latter is almost universally represented by the Arrhenius equation:

$$k(T) = A \exp\left(\frac{-E_a}{RT}\right) \tag{2}$$

Where A (min^{-1}) is the frequency factor, R is the gas constant, E_a is the activation energy (kJ mol^{-1}).

Substituting the Eq. (2) into Eq. (1) we obtain:

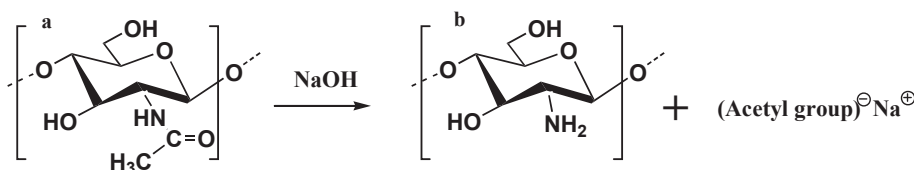$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right) \cdot f(\alpha) \tag{3}$$

Fig. 1. The structure of chitin (a) and chitosan (b).