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Influence of the degree of substitution in biopolymeric Schiff bases on the kinetic of thermal decomposition by non-isothermal procedure

Luciana Simionatto Guinesi, Éder Tadeu Gomes Cavalheiro *

Departamento de Química e Física Molecular, Instituto de Química de São Carlos, Universidade de São Paulo, Avenida do Trabalhador São-carlense, 400, CEP 13566-590, São Carlos, SP, Brazil

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Abstract

The influence of the degree of substitution (DS) in biopolymeric Schiff bases prepared from chitosan and salicylaldehyde on the kinetic of its thermal decomposition by non-isothermal procedure was evaluated. Applying the isoconversional Flynn–Wall–Ozawa method on the dynamic TG/DTG curves, the activation energy, E, and the pre-exponential factor, A, presented a non-linear growing dependence upon the DS of biopolymeric Schiff bases. To fractional conversion within the $0.05 \leq \alpha \leq 0.50$ interval, the average values to the $E = 118.5 \pm 4.6$, 141.9 ± 6.1, 172.9 ± 5.6, 196.9 ± 7.6 and 248.7 ± 6.0 kJ mol^{-1} and $\log A = 12.53 \pm 0.55$, 13.73 ± 0.35, 14.92 ± 0.37, 16.10 ± 0.44 and 17.47 ± 0.68 min^{-1} are obtained for samples with DS = 0, 21.9, 35.9, 44.5 and 60.4%, respectively. From E and $\log A$ values and the generalized time θ, the JMA (Johnson–Mehl–Avrami) and SB (Sesták–Berggren) seem to be the most suitable kinetic models, $f(\alpha)$, in describing physicogeometrically the thermal decomposition for solid unmodified chitosan (DS = 0) and the biopolymeric Schiff bases (DS = 21.9 and 60.4%), respectively.

Keywords: Chitosan; Biopolymeric Schiff bases; Thermal decomposition; Non-isothermal kinetic

1. Introduction

1.1. Biopolymeric Schiff bases

Chitin is a biodegradable and nontoxic polysaccharide widely spread among marine and terrestrial invertebrates. It is usually obtained from waste materials of the sea food-processing industry, mainly crab, shrimp, prawn and lobster shells [1,2]. The chitosan is usually prepared from chitin by chemical *N*-deacetylation [3,4]. Chitin and chitosan are closely related since both are linear polysaccharides containing 2-acetamido-2-deoxy-D-glucopyranose (*GlcNAc*) and 2-amino-2-deoxy-D-glucopyranose (*GlcN*) units joined by $\beta(1 \rightarrow 4)$ glycosidic bonds.

The ratio of *GlcNAc* in relation to the *GlcN* units is defined as the degree of *N*-acetylation (DA) and differentiates chitin (DA > 0.5) from chitosan (DA ≤ 0.5). However, this definition is just an approach and in practice the difference is also defined by solubility in aqueous acidic medium, in which chitosan is soluble while chitin is not [5].

In chitosan structure predominates the *GlcN* residues whose free amino groups at C-2 position allows its solubility in acidic medium [6,7] and permits reactions with several substituents resulting in a wide series of modified biopolymers with a large spectrum of applications [8]. Among these substituted biopolymers there are the Schiff bases, obtained by the reactions of the free amino groups of chitosan with an active carbonyl compound such as aldehyde or ketone [9,10].

These modified biopolymers can be used in applications such as removal of heavy metals from waters and other decontaminations, in inorganic and analytical chemistry as chelating agents and as electrode modifiers in electroanalysis [11].

The extension of Schiff base formation has been called degree of substitution, DS, defined as the number of free amino groups in relation to the Schiff bases on the substituted biopolymeric matrix, represented in Fig. 1. As the DS is not 100% the resulting material should present a mix of the original chitosan and the Schiff base properties.

The preparation and the thermal behavior of the biopolymeric Schiff bases from chitosan and salicylaldehyde and its

* Corresponding author. Tel.: +55 1633738054; fax: +55 1633739987.
E-mail address: cavalheiro@iqsc.usp.br (É.T.G. Cavalheiro).

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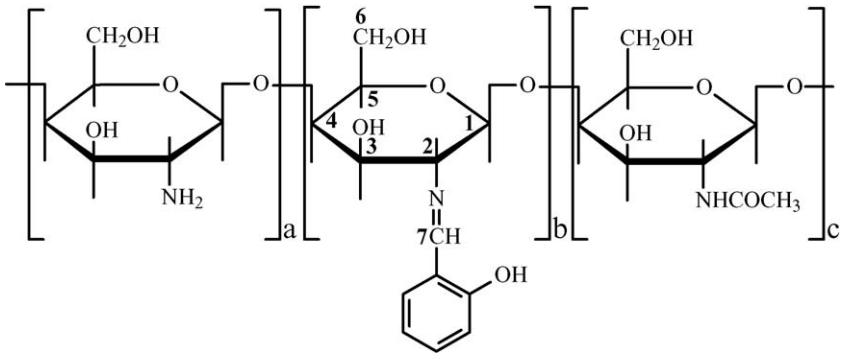

Fig. 1. Representative structure for biopolymeric Schiff bases prepared by the reaction of free amino groups from 2-amino-2-deoxy-D-glucopyranose (*GlcN*) units and salicylaldedyde. The ratio of Schiff base (b) in relation to the unreacted amino groups (a) is called degree of substitution (DS).

substituted derivatives 5-bromo, 5-chloro, 5-nitro, 5-methyl and 5-methoxy with DS = 17.1, 4.6, 5.3, 19.5, 34.1 and 68.5%, respectively have previously been reported [12,13].

The optimization of reactional parameters in order to improve the DS in the reaction of chitosan and salicylaldehyde has also been described. These studies leaded to DS as higher as 60% [14].

The main objective of the present work is to investigate the influence of the degree of substitution in biopolimeric Schiff bases from chitosan and salicylaldehyde on the activation energy, E, and the pre-exponential factor, A, regarding its thermal decomposition by non-isothermal procedure. In addition, changes in the thermal decomposition kinetic model, $f(\alpha)$, were also investigated as a function of DS.

The kinetic aspects for E and A determination using the isoconversional method of Flynn, Wall and Ozawa has widely been described [15–20] and they are not presented here. Differently, the $f(\alpha)$ determination is a relatively new approach which is detailed below.

1.2. Kinetic model determination

The mathematical description of the data from a single step solid state decomposition is usually defined in terms of a kinetic triplet: activation energy, E, pre-exponential factor, A, and an algebraic expression of the kinetic model as a function of the fractional conversion α, $f(\alpha)$, which can be fitted to the experimental data as follows [15]:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{1}$$

For dynamic data obtained at a constant heating rate, $\beta = dT/dt$, this new term is inserted in Eq. (1) to obtain

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{2}$$

where R is the gas universal constant (8.314 J K^{-1} mol^{-1}).

Compared with isothermal experiments, non-isothermal runs are more convenient to carry out because it is not necessary to perform a sudden temperature jump of the sample at the beginning [21].

Once the activation energy and the pre-exponential factor have been determined, it is possible to find the kinetic model, $f(\alpha)$, that best describes measured set of thermogravimetric data.

The kinetic rate equation at infinite temperature is obtained by using the concept of the generalized time, θ, introduced by Ozawa [16,22]:

$$\theta = \int_0^t \exp\left(-\frac{E}{RT}\right) dt \tag{3}$$

where R is the gas constant and θ denotes the reaction time taken to attain a particular α at infinite temperature. First differentiation of Eq. (3) gives [23]

$$\frac{d\theta}{dt} = \exp\left(-\frac{E}{RT}\right) \tag{4}$$

Combining Eq. (1) with Eq. (4) the following expression is obtained [23–25]:

$$\frac{d\alpha}{d\theta} = A f(\alpha) = y(\alpha) \tag{5}$$

where $d\alpha/d\theta$ corresponds to the generalized reaction rate obtained by extrapolating the reaction rate in real time, $d\alpha/dt$, to infinite temperature [23,24].

The integrated form of Eq. (5) after rearrangement gives [24]

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \int_0^\theta d\theta = A\theta \tag{6}$$

By combining Eqs. (5) and (6), we obtain the following general expression for the $z(\alpha)$ function [26]:

$$\left(\frac{d\alpha}{d\theta}\right) \theta = f(\alpha) g(\alpha) = z(\alpha) \tag{7}$$

However, $y(\alpha)$ and $z(\alpha)$ requires the knowledge of θ which is defined by Eq. (3) that involves the time dependence of temperature. From the kinetic data under a linear heating rate of β, the value of θ at a given α can be defined as [24]

$$\theta = \frac{1}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{E}{\beta R} \int_x^\infty \frac{\exp(-x)}{x^2} dx = \frac{E}{\beta R} p(x) \tag{8}$$

The function $p(x)$, where $x = E/RT$, cannot be expressed in a closed form, although several convergent series exist for its approximation. For example, the fourth rational Senum and Yang [27] corrected by Flynn [19], allows an accuracy of better than 10^{-5}% for $E/RT = 20$. So, $p(x)$ can be expressed by

$$p(x) = \frac{e^{-x}}{x}\pi(x) \quad (9)$$

where

$$\pi(x) = \frac{x^3 + 18x^2 + 86x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (10)$$

Because the $y(\alpha)$ and $z(\alpha)$ functions are invariable with respect to temperature or heating rate, being quite sensitive to subtle changes in the kinetic model $f(\alpha)$, they can be conveniently used as suitable tools for kinetic model determination [25].

2. Experimental

2.1. Chitosan purification

The chitosan used in this work was of technical grade with medium molecular weight from crab shells (Aldrich/USA). The purification was attained by the dissolution of the crude commercial product (approximately 1 g) in 300 mL of dilute 0.5 mol L^{-1} acetic acid solution. The dissolution of the polysaccharide was assured by stirring the initial suspension for 12 h and precipitated in the hydrogel form by carefully adding concentrated NH_4OH. The chitosan hydrogel was washed with water until neutrality, followed by ethanol. The final product was dried at 60 °C under reduced pressure. The purified sample was kept under reduced pressure in desiccator over silica gel. The DA = 11.2% was determined by ^{1}H NMR [14].

2.2. Preparation of the biopolymeric Schiff bases

Salicylaldehyde (Aldrich) was used without additional purification. The biopolymeric Schiff bases were synthesized by dissolving 400 mg of the purified chitosan with 25.0 mL of dilute 0.15 mol L^{-1} acetic acid solution in a reaction vessel immersed in a thermostated bath at 25 °C for 12 h under continuous stirring in order to assure its dissolution in a hydrogel form. Then, a desired amount of salicylaldehyde previously dissolved in 10.0 mL of ethanol was added to the chitosan solution. This mixture was let to react varying the set of experimental conditions such as mol ratio of salicylaldehyde:free amino group, temperature and time of reaction. Deep yellow gels revealed the formation of the Schiff base on the biopolymeric matrix. The resulting gels were collected by filtration, washed several times with ethanol to remove any unreacted aldehyde, dried at 60 °C under reduced pressure yielding yellow powders that were kept in a desiccator over silica gel. The experimental conditions were: 1.00:1.00 mol ratio, 25.0 °C, 12 h; 1.50:1.00 mol ratio, 25.0 °C, 12 h; 1.50:1.00 mol ratio, 45.0 °C, 12 h; 1.50:1.00 mol ratio, 55.0 °C, 18 h yielding the samples with DS as 21.9, 35.9, 44.5 and 60.4% determined by ^{1}H NMR [14].

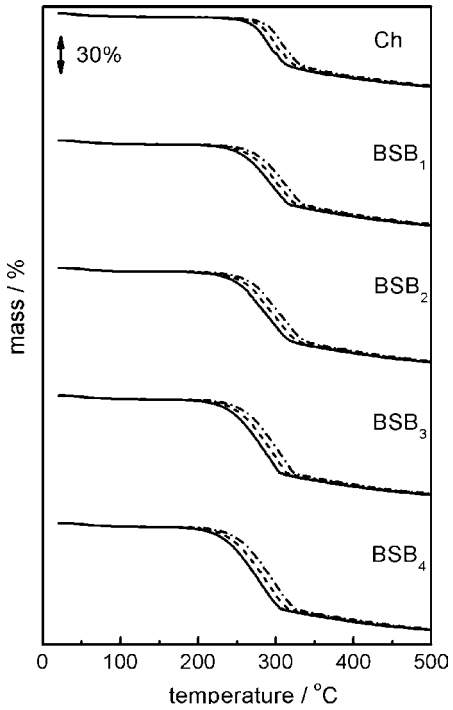

Fig. 2. TG curves of chitosan, Ch, and biopolymeric Schiff bases, BSB_1, BSB_2, BSB_3 and BSB_4 with DS = 0, 21.9, 35.9, 44.5 and 60.4%, respectively under nitrogen atmosphere at 5 °C min^{-1} (—), 10 °C min^{-1} (- - - -) and 20 °C min^{-1} (- · - · -).

The samples were then characterized as described elsewhere [12,14].

2.3. Thermogravimetry

Thermogravimetriy (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) were performed in a SDT-Q600 simultaneous TG/DTA modulus from TA Instruments. The TG/DTG–DTA curves of the chitosan and biopolymeric Schiff bases were carried out under nitrogen atmosphere (50 mL min^{-1}), alumina crucible, sample mass around 7 mg and heating rates of 5, 10 and 20 °C min^{-1} from 25 to 900 °C. The E and $\log A$ kinetic parameters were calculated using the software TA Advantage Specialty Library from TA Instruments.

3. Results and discussion

The main bands observed in the IR spectra and the thermal behavior under air atmosphere of the chitosan and its Schiff bases were previously reported [12–14].

The TG curves under nitrogen atmosphere for chitosan and biopolymeric Schiff bases at 5, 10 and 20 °C min^{-1} from room temperature to 500 °C are presented in Fig. 2 and the results at 5 °C °min^{-1} are in Table 1. The first thermal event can be related to the dehydration step for all samples in correspondence with endothermic peaks in the DTA curves. The second step can be related to the thermal decomposition of *GlcNAc*, *GlcN* and *GlcN-Schiff base* in the polymeric matrix of unmodified and modified chitosan samples in correspondence with exothermic peaks in the DTA curves as described [28]. The mass losses are pro-

Table 1
Data taken from TG/DTA curves corresponding to the dehydration and decomposition of chitosan and biopolymeric Schiff bases with different DS under nitrogen atmosphere at 5 °C min^{-1}

Compound (DS, %)	Process	TR (°C)	Mass loss (%)	Tp (°C)
Ch (0)	Ch·nH$_2$O → Ch + nH$_2$O	25–112	3.20	38.2 (endo)
	Ch → CR	201–330	40.0	295 (exo)
	CR decomposition	331–900	25.0	–
BSB$_1$ (21.9)	BSB$_1$·nH$_2$O → BSB$_1$ + nH$_2$O	25–110	3.19	41.5 (endo)
	BSB$_1$ → CR	195–324	49.8	280 (exo)
	CR decomposition	324–900	23.0	–
BSB$_2$ (35.9)	BSB$_2$·nH$_2$O → BSB$_2$ + nH$_2$O	25–111	3.20	39.4 (endo)
	BSB$_2$ → CR	187–318	56.5	272 (exo)
	CR decomposition	319–900	22.5	–
BSB$_3$ (44.5)	BSB$_3$·nH$_2$O → BSB$_3$ + nH$_2$O	25–110	3.22	41.5 (endo)
	BSB$_3$ → CR	170–305	60.1	268 (exo)
	CR decomposition	306–900	20.3	–
BSB$_4$ (60.4)	BSB$_4$·nH$_2$O → BSB$_4$ + nH$_2$O	25–107	3.18	40.3 (endo)
	BSB$_4$ → CR	163–307	67.3	255 (exo)
	CR decomposition	308–900	19.2	–

Ch, unmodified chitosan; BSB, biopolymeric Schiff base; TR, temperature range; Tp, peak temperature; endo, endothermic process; exo, exothermic process; CR, carbonaceous residue.

portional to DS. The biopolymeric Schiff bases are thermally less stable than unmodified chitosan. This behavior was also observed for biopolymeric Schiff bases prepared from chitosan and benzaldehyde derivative [29]. The third thermal event presented a continuous mass loss related to the slow decomposition of a carbonaceous residue. This product was also observed earlier for Schiff bases prepared from chitosan and salicylaldehyde derivatives [13]. These curves were used for the evaluation of the kinetic triplet: E, A and $f(\alpha)$.

DTA curves for the samples are presented in Fig. 3. Is possible to see the exothermic decomposition peak, whose maximum is displaced to lower temperatures while the DS increases. The temperature differences in the peaks is higher as higher the DS, changing from 2.9 °C for chitosan up to 4.7 °C for the BSB4 which presented the highest DS in the set of samples.

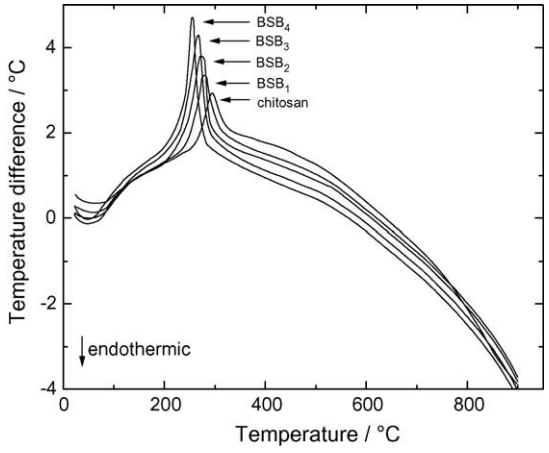

Fig. 3. DTA curves of chitosan and biopolymeric Schiff bases, BSB$_1$, BSB$_2$, BSB$_3$ and BSB$_4$ with DS = 0, 21.9, 35.9, 44.5 and 60.4%, respectively under nitrogen atmosphere at 5 °C min^{-1}.

3.1. Calculation of the activation energy and pre-exponential factor

The kinetic parameters E and log A related to the thermal decomposition of *GlcNAc*, *GlcN* and *GlcN-Schiff base* residues from chitosan and biopolymeric Schiff bases were obtained applying the isoconversional method of Flynn, Wall and Ozawa [15–20] to the mass losses defined by TG/DTG curves at 5, 10 and 20 °C min^{-1} under nitrogen atmosphere (Fig. 2). The reaction limits employed are presented in Table 2.

Table 2
Reaction limits taken from TG/DTG curves to obtain the kinetic parameters E and log A regarding the thermal decomposition of *GlcNAc*, *GlcN* and *GlcN-Schiff base* residues from chitosan and biopolymeric Schiff bases

Compound (DS, %)	Heating rate (°C min^{-1})	TR (°C)	Mass loss (%)
Ch (0)	4.98	201–330	39.5
	9.99	215–339	40.6
	19.50	224–348	41.2
BSB$_1$ (21.9)	5.10	195–324	49.1
	10.02	202–333	49.3
	19.99	211–342	49.0
BSB$_2$ (35.9)	4.98	187–318	55.5
	10.50	194–327	55.9
	19.50	203–336	55.6
BSB$_3$ (44.5)	4.99	170–305	59.3
	9.99	184–315	59.5
	20.00	193–324	60.7
BSB$_4$ (60.4)	5.00	163–307	66.4
	9.99	174–315	67.1
	19.50	184–324	66.5

Ch, unmodified chitosan; BSB, biopolymeric Schiff base; TR, temperature range.

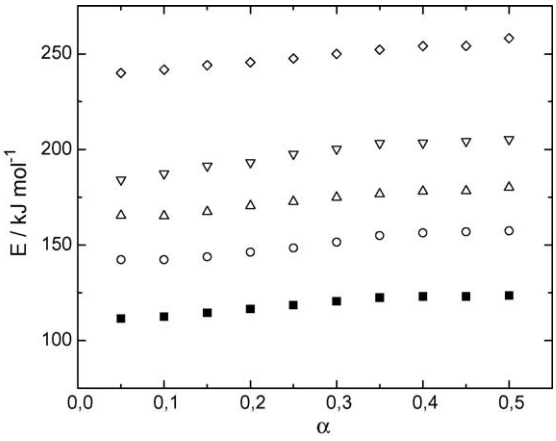

Fig. 4. Dependence of activation energy on conversion (α) for chitosan (■), BSB_1 (◯), BSB_2 (△), BSB_3 (▽) and BSB_4 (◊).

A graph representing the dependence of activation energy on conversion (α) for each sample is presented in Fig. 4. These curves suggest that no change occurs in the decomposition mechanism during the decomposition of the samples.

To each fixed fractional conversion, α, the activation energy, E, could be calculated from the slop of a $\log \beta$ versus $1000/T$ plots and its correspondent $\log A$. The obtained results must be within the limit $28 \leq E/RT \leq 50$ in order to permit be use the Doyle approximation to $p(x)$ [30]. Then, for chitosan and biopolymeric Schiff bases the dependences of the activation energy and the DTA peak temperature as a function of the degree of substitution are presented in Fig. 5, where is possible to note that E grows not linearly while the DTA peak temperature presented a linear dependence ($y = 295 + 0.64\,x$; $r = -0.9973$; $n = 5$) upon the DS. In fact, the higher degree of substitution, the higher is the activation energy while the peak temperature decreases during the thermal decomposition of biopolymeric Schiff bases in relation to the unmodified chitosan. This is discussed below considering the kinetic models for each sample.

3.2. Determination of the kinetic model

To the data from TG/DTG curves at 5 °C min^{-1} under nitrogen atmosphere, the physicogeometric mechanism or kinetic

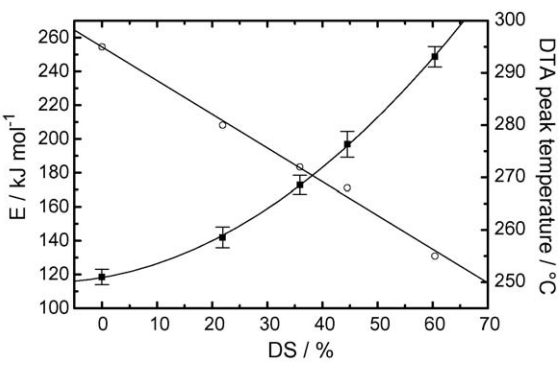

Fig. 5. Dependence of activation energy, E (■) and DTA decomposition peak temperature (◯), with the substitution degree.

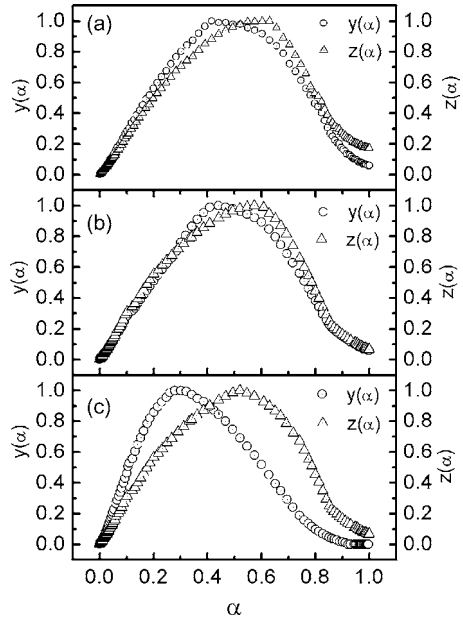

Fig. 6. The normalized $y(\alpha)$ and $z(\alpha)$ functions regarding the thermal decomposition of the samples: unmodified chitosan (a), biopolymeric Schiff bases with DS = 21.9% (b) and 60.4% (c).

model, $f(\alpha)$, to the thermal decomposition of *GlcNAc*, *GlcN* and *GlcN-Schiff base* residues from chitosan and biopolymeric Schiff bases has been determined. For this purpose, the kinetic rate equation at infinite temperature, Eq. (3), obtained by using the concept of generalized time θ, seems to be useful [16,22]. However, this determination can be reached by extrapolating the kinetic data recorded in real time under any temperature profile, $d\alpha/dT$, to infinite temperature, $d\alpha/d\theta$, which corresponds to the generalized reaction rate, Eq. (5) [23,24]. The extrapolation requires the knowledge of α and θ. The fractional conversion α can be calculated by partial integration of DTG curve [26]. The generalized time θ can be calculated using the Eqs. (8)–(10) [24].

Knowing α and θ, it is possible to define the $y(\alpha)$ and $z(\alpha)$ functions calculated by the Eqs. (5) and (7) whose shape and maximum values can be used as a guide in the kinetic model determination [24,31,32]. Fig. 6 presented the $y(\alpha)$ and $z(\alpha)$ functions normalized within the $\langle 0, 1 \rangle$ interval regarding the thermal decomposition of the *GlcNAc*, *GlcN* and *GlcN-Schiff base* residues from unmodified chitosan and the biopolymeric Schiff bases with DS = 21.9 and 60.4%. The $z(\alpha)$ function present its maximum, α_z^*, located at 0.63, 0.57 and 0.52 for samples with DS = 0, 21.9 and 60.4%, respectively. The $y(\alpha)$ function present its maximum, α_y^*, located at 0.42, 0.44 and 0.30 for samples with DS = 0, 21.9 and 60.4%, respectively. The value of α_y^* is always lower than α_z^* [26].

If $y(\alpha)$ exhibits its maximum in $0 < \alpha_y^* < \alpha_p$ interval (where α_p is the fractional extent corresponding to the maximum rate $d\alpha/dt$), the Johnson–Mehl–Avrami (JMA) or the Sesták–Berggren (SB) are the most probable kinetic models [25,31,32]. However, the validity of the JMA model can easily be verified by checking the maximum α_z^* that falls into the $0.61 \leq \alpha_z^* \leq 0.65$ interval [26] satisfying the condition only for unmodified chitosan. The JMA model is described by the kinetic

equation: $f(\alpha) = n(1-\alpha)[-\log(1-\alpha)]^{1-(1/n)}$. The kinetic exponent n is calculated from the relation: $n = 1/(1 + \log(1-\alpha_y^*))$, yielding $n = 2.20$ [31]. The JMA kinetic equation was developed to describe the formal theory of nucleation and growth and it can be applied to the description of non-isothermal TA data when the entire nucleation process takes place during early stages of the transformation and becomes negligible afterwards [31].

Otherwise, the biopolimeric Schiff bases satisfied the conditions for SB model described by the kinetic equation: $f(\alpha) = \alpha^M(1-\alpha)^N$. The kinetic parameter N corresponds to the slope of the linear dependence of $\log[(d\alpha/dt)\exp(E/RT)]$ versus $\log\lfloor\alpha^p(1-\alpha)\rfloor$ plot in $0.2 < \alpha < 0.8$ interval that yields $N = 1.0$ and 1.5 for samples with DS = 21.9 and 60.4%, respectively. The kinetic exponent M corresponds to the relation $M = pN$, where $p = \left\lfloor \alpha_y^*/(1-\alpha_y^*) \right\rfloor$, that yields $M = 0.78$ and 0.62 for samples with DS = 21.9 and 60.4% respectively [31,33–35]. The n, M and N results are in agreement with the α_y^*–α_z^* plots reported [25]. The increasing value of the kinetic exponent M indicates a more important role of the product on the overall kinetics with an autocatalytic behavior. The higher value of the kinetic exponent $N > 1$ means increasing complexity of the process and can be caused, for example, by the influence of surface nucleation. In fact, the two-parameter SB model includes the JMA as a special case whose applicability involves a narrowest limit for α_y^*–α_z^* values in relation to the SB [25]. However, the physical meaning attributed for M–N should not go beyond those described above, unless more detailed conclusions concerning the decomposition mechanism should be based on other types of complementary evidence, including microscopic observations and all other relevant information [26].

Knowing the α–T dependence and the kinetic triplet: E, A, and $f(\alpha)$, the simulated $d\alpha/dT$ versus T plot can be calculated using the Eq. (2) whose proximity with the experimental DTG curve confirms the JMA and SB as the most probably kinetic models for unmodified chitosan and the biopolymeric Schiff bases, respectively. Fig. 7 presents the simulated and experimental DTG curves at 5 °C min^{-1} normalized within the ⟨0, 1⟩ interval.

3.3. Final considerations

Considering Fig. 5 there is apparently controversial behavior between the activation energy and the stability of the samples, since the decomposition temperature is lower for biopolymeric Schiff bases with higher DS while the E increases. Since the decomposition occurs by an exothermic process [36], the energy liberated seems to be used in the decomposition itself. As higher the DS of the sample more energy is liberated and lower will be the DTA peak decomposition temperature.

Of course the self-heating (or self-cooling) of the sample can cause errors in the E calculation [37] if the magnitude of the temperature increase (or decrease), ΔT, is higher enough. In present case the ΔT, the temperature increase, is from 2.9 to 4.7 °C for chitosan and BSB_4 respectively at 270 °C, approximately the mean decomposition peak temperature in Fig. 3. This represents an increase of only 1.1–1.7% in the temperature to which the system is submitted, that is apparently not enough to promote significant changes in the calculated E.

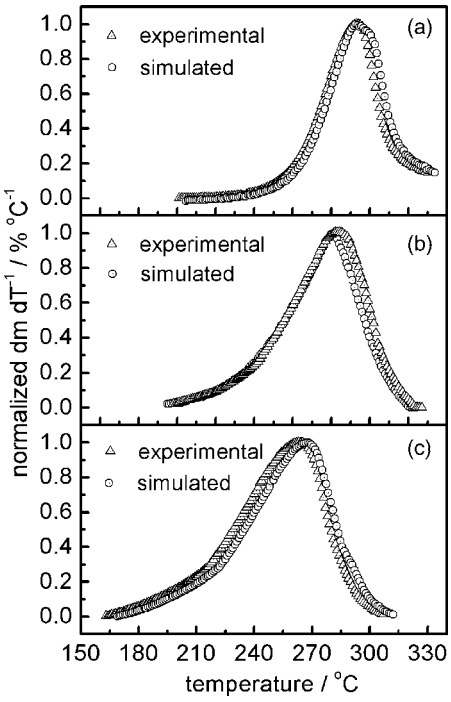

Fig. 7. Simulated and experimental DTG curves at 5 °C min^{-1} under nitrogen atmosphere regarding the thermal decomposition of the samples: unmodified chitosan (a), biopolymeric Schiff bases with DS = 21.9% (b) and 60.4% (c).

This is in agreement with the SB model, which is based in a self-catalytic decomposition process [26], the liberated energy is responsible for the catalytic effect.

4. Conclusions

The both activation energy, E, and the pre-exponential factor, A, regarding the thermal decomposition of the chitosan and its Schiff bases derivative from salicylaldehyde presented an exponential growing dependence upon the degree of substitution in biopolymeric matrix. It can be seen from the resemblance between experimental and simulated DTG curves that the JMA and SB are the most suitable kinetic models in describing physicogeometrically the decomposition for unmodified chitosan and the biopolymeric Schiff bases with DS = 21.9 and 60.4%, respectively.

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