Bulgarian Chemical Communications, Volume 58, Special Issue A (pp. 54-58) 2026 DOI: 10.34049/bcc58.A.SN-10

Kinetic study of the pyrolysis of chitosan-zeolite composite

K. Zafirova[1], D. Zvezdova[2*]

[1]*Medical University "Prof. Dr. Paraskev Stoyanov", Faculty of Pharmacy, Varna, Bulgaria*
[2]*Burgas State University "Prof. Dr, Assen Zlatarov", Faculty of Public Health and Health Care, Burgas, Bulgaria*

Received: September 04, 2025; Revised: December 01, 2025

Decomposition thermal analysis of chitosan-zeolite composite was carried out. The decomposition of the complex solid phase was studied using non-isothermal thermogravimetry. A complex optimization criterion for most accurate decomposition was developed. The data obtained on the basis of the complex method and complex criteria showed that most relevant is the separation of the complex process into three sub-processes. The advantage of the direct complex thermogravimetry method compared to other methods was shown. The results of the decomposition identification were analyzed.

Keywords: Chitosan–zeolite composite, pyrolysis, kinetics

INTRODUCTION

The first applications of chitosan (CS) have been in food and nutrition, material science, pharmacology, cosmetology, medicine, agriculture, and water treatment [1-4]. Chitosan is a polysaccharide corresponding to linear copolymers of 2-amino-2-deoxy-D-glucan and 2-acetamido-2-deoxy-D-glucan linked by a β-(1-4), which can be found in the exoskeletons of crustaceans and insects and in the cell walls of fungi and microorganisms [5]. Its main derivative, chitosan, obtained by deacetylation of CS, consists of the randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). CS contains a low amount of 2-amino-2-deoxyglucose and hence it is less soluble in acidic solvents, whereas CS contains a smaller amount of N-acetyl-2-amino-2-deoxy-D-glucose and is therefore soluble in acidic solvents [6-8]. The deacetylation process consists of the removal of the acetyl groups from the CS molecular chain, leaving behind a complete amino group (NH_2). The properties of CS are closely linked to the chemical reactivity of these amino groups, for example, their protonation in acidic medium leads to antifungal or antimicrobial activities, since cations can bend to the anionic sites in proteins.

CSZ (chitosan-zeolite) is the most studied composite of chitosan [9, 10]. It has been shown that the nanocomposite has improved properties, such as mechanical strength, gas barrier, and thermal stability, compared to pure CS [11]. This was related to the excellent dispersion of the nanoclay and its strong interaction with the CS matrix.

Whatever the method used, these polymers have a certain limitation in many engineering applications due to their low mechanical properties, moisture resistance, and thermal stability. These limitations are overcome by the recent development of a new class of materials, named biocomposite/ bionanocomposite materials, in which these biopolymers have been used as a matrix [12]. Unlike other nanofillers, biopolymer/clay biocomposites have been widely studied and applied in several research fields, because clays are available, cheap, and their intercalation chemistry is well-known [13, 14]. Thermal behavior can be studied by using certain physicochemical techniques, including DSC (differential scanning calorimetry), TGA (thermogravimetric analysis), DTG (differential thermal analysis), DMA (dynamic mechanical analysis), and other thermal analysis methods. Thermogravimetric analysis (TGA/DTA) has been widely used by many authors to study the kinetics of thermal degradation under isothermal and dynamic conditions, both in air and in nitrogen.

In most cases, the data can be used to determine the degradation mechanism and kinetic triplet evaluation (*E*a: activation energy, A: preexponential factor, conversion function). This value has been linked to the presence of intermolecular and intramolecular hydrogen bonds in the CS structure and to the diffusion phenomenon.

The literature lacks scientific studies addressing the pyrolysis kinetics of chitosan–zeolite composite materials. Consequently, the present research focuses on determining the kinetic parameters governing the thermal degradation of these structural composites.

---

* To whom all correspondence should be sent:
E-mail: *zvezdova@abv.bg*

METHODOLOGY

The thermogravimetric experiments were performed on the STA 449 F3 Jupiter complex thermal analysis apparatus (Netzsch - Germany). Experimental data were obtained for the temperature range of 293.15-1073.15 K at four heating rate settings β = 4.0, 6.0, 9.0 and 12.0 deg min^{-1}. The sample masses were about 5 mg. The purging was carried out with artificial air at a rate of 20 ml min^{-1}. Data from 1000 points were collected for each experiment at intervals of 0.1 s. Each point included time data from the beginning of the experiment, TG, DTG and DSC data. The experimental data were filtered with a two-way filter.

The quality of decomposition, for all experiments collectively and for each individual experiment, was evaluated using the relative error:

$$\gamma = \frac{A^{\text{calc}} - A^{\text{exp}}}{A^{\text{exp}}_{\text{max}} - A^{\text{exp}}_{\text{min}}} 100, \% \qquad (1)$$

where A represents the degree of conversion α, the rate of conversion with respect to time $d\alpha/dt$ or with respect to temperature $d\alpha/dT$.

The results of the non-isothermal analysis of a chitosan sample for β=12 deg min^{-1} are shown in Fig. 1. The thermogravimetric (TG) analysis indicates that the process consists of three main stages of mass loss.

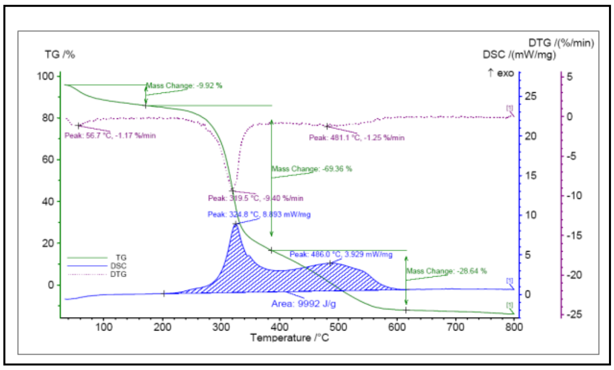

Fig. 1. TG, DTG and DSC curves of CSZ composite obtained at β=12 deg min^{-1}

Chitosan (CS) was extracted from Black Sea crab shells through standard chemical treatment involving demineralization with hydrochloric acid, deproteinization with sodium hydroxide, and deacetylation in concentrated alkali solution. Before the preparation of nanocomposites, the CS matrix was dissolved in a 1% (v/v) solution of acetic acid, and the filler (Z) was swollen in H_2O under magnetic stirring for 30 min.

For the experimental TG data of chitosan derived from Black Sea crabs, a pseudo-isoconversional analysis was performed using both differential and integral approaches, revealing that the former one exhibits higher sensitivity. Optimal parameters for Distributed Activation Energy Model (DAEM) identification were obtained through the comprehensive approach for the conversion range of $0.1 \leq \alpha \leq 0.9$. For each of the identified and parameterized subprocesses, thermal parameters—including the changes in entropy (ΔS), enthalpy (ΔH), Gibbs free energy (ΔG), and others—were calculated and evaluated. Owing to the good adequacy of the results, this approach was applied in our investigations of products and processes involving chitosan [15].

TG and DSC studies were conducted in the temperature range of 293.15-1073.15 K. For all membranes, three main peaks of mass loss were observed, the first peak (328.85 K) resulting from water loss. This stage is endothermic and occurs from the start of heating up to 393.15 K, with a mass loss of 9.92%, consisting mainly of water physically adsorbed on the surface of the material. This process was not of interest in the present study. The second (653.15 K) and the third (788.15 K) peak correspond to sample degradation. In general, intermolecular and intramolecular hydrogen bonding can contribute to increasing the thermal stability of the membrane. In the second main stage, degradation processes of CSZ take place, with a mass loss of 68.36%, ending at approximately 653.15 K. It is attributed to further deacetylation, cleavage of glycosidic bonds, and the subsequent oxidation of the residues. In the third stage, the mass of the sample begins to change at a slower rate and ends at approximately 1124.15 K with a mass loss of 28.64%. This peak indicates the occurrence of oxidation processes and corresponds to the CS decomposition reactions and the formation of volatile compounds formed by oxidation of carbon residues.

DSC analysis shows that the homogeneous nature of CS and zeolite yields relatively pronounced endothermic peaks. An increase in the endothermic peak is observed upon the introduction of zeolite. This result indicates that CSZ membranes are more stable at high temperatures in comparison to those from crab CS.

The holographs of the α–T and v_α–T lines (where v_α ≡ dα/dτ) after filtering the TG data are shown in Fig. 2. The figure does not display the stage of evaporation of adsorbed water nor the probable oxidation process above 1123.15 K, as these are beyond the scope of the present study. The uniform shift of the dependencies between the degree of conversion α and temperature T, and between the conversion rate v_α and T with increasing heating rate β are clear indicators of data's validity. The nature of the curves suggests that the complex process consists of two or more subprocesses.

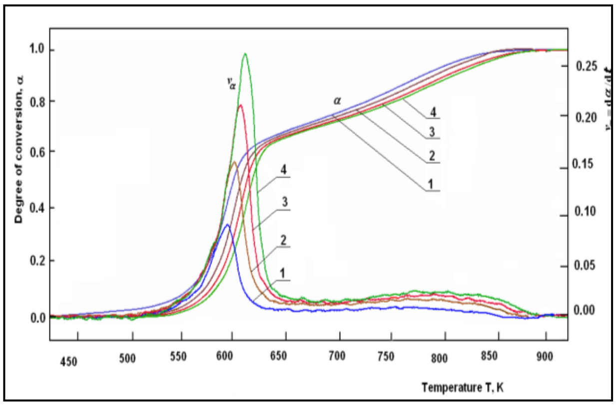

Fig. 2. Change in the degree of conversion and the rate of conversion with temperature (1, 2, 3, 4 correspond to heating rates $\beta = 4$, 6, 8, and 12 °C/min, respectively).

Similar conclusions can be drawn from the graphs in Fig. 1.

Identification and parameterization were performed using appropriate software [16]. The process was carried out with TG data from the range $0.0000 \le \alpha \le 1.0000$ and included 970 evenly spaced points along the α–T curves [16]. The instantaneous heating rates were taken into account.

New formulas were used for calculating the Arrhenius criterion [16]. A complex criterion was applied to evaluate the quality of the decomposition analysis, which is a function of the standard deviations of the conversion degree α and its rate with respect to time or temperature. Kinetic analysis was conducted with different numbers of subprocesses (Sp). The results of the kinetic analysis are presented in Table 1.

Table 1 shows that the most adequate results are obtained for decomposition involving three subprocesses, described by the kinetic models F1(α) [A1(α)], D5(α), Ap(α) with differential f(α) and integral g(α) forms, respectively:

$$f_{A_1}(\alpha) = (1-\alpha). \qquad g_{A_1}(\alpha) = -\ln(1-\alpha);$$
$$f_{D_5}(\alpha) = (3/2)(1-\alpha)^{4/3}\left[(1-\alpha)^{-1/3}-1\right]^{-1},$$
$$g_{D_5}(\alpha) = \left[(1-\alpha)^{-1/3}-1\right]^{2}; \tag{2}$$
$$f_{Ap}(\alpha) = P(1-\alpha)[-\ln(1-\alpha)]^{p}$$
$$g_{Ap}(\alpha) = \frac{\left[-\ln(1-\alpha)\right]^{p}}{P(1-p)}; \qquad P = \left|\frac{1}{p-1}\right|$$

Table 1. Results from identification by a complex method for thermal degradation of CSZ

Result \ Process	Sub-process 1	Sub-process 2	Sub-process 3
Type of model	D5	Ap	A1
Activation energy, E_a (kJ/mol)	176321.4	70072.73	312112.7
Preexponential factor *A* (1/min)	6.0713E +10	389750.3	9.0454E +26
Exponent	-	0.453603	-
Weight coefficient	0.328998	0.375598	0.295404

Global best complex criteria	0.00018
R^2 (α)	0.99901
R^2 dα/dt	0.9915
Standard deviation - α	0.011204
Standard deviation - dα/dt	0.008175

From the experimental TG data, the activation energies *E* and the pre-exponential factor *A* were calculated for various evenly distributed conversion degrees from 0.1 to 0.9. The formulas from the FWO method were used:

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

The activation energy (*E*a) can be obtained from the plot of log β against 1/*T* for a fixed degree of conversion, since the slope of such line is given by -0.4567 *E*a/R. The preexponential factor, A can be obtained from the equation:

$$A = \frac{-\beta E_0}{RT_{max}^2 f'(\alpha_{max})} \exp\left(\frac{E_0}{RT_{max}}\right) \tag{4}$$

The graphical dependencies for the calculations by the FWO method are shown in Fig. 3. For both products, the obtained results exhibit a high correlation coefficient.

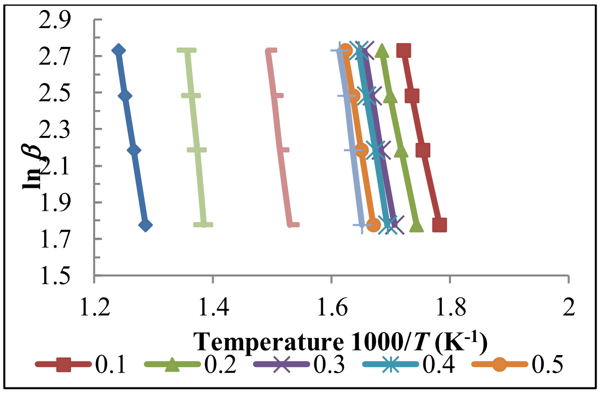

Fig. 3. Plots of ln β *vs.* 1000/*T* for the thermal degradation of CSZ composite at different conversion rates α (FWO method).

Table 2. Kinetic parameters obtained for CS and CSZ using FWO methods

	CSZ			CS		
α	E_a (KJ/mol)	A (1/min)	R	E_a (KJ/mol)	A (1/min)	R
0.1	386.66	7.43×10^{25}	0.9972	284.31	7.43×10^{25}	0.9982
0.2	349.34	1.51×10^{26}	0.9987	294.07	1.518×10^{26}	0.9991
0.3	362.99	7.65×10^{29}	0.9982	341.33	7.664×10^{29}	0.9993
0.4	421.79	2.10×10^{31}	0.9952	359.99	2.191×10^{31}	0.9997
0.5	385.75	5.43×10^{31}	0.9967	369.55	5.43×10^{31}	0.9997
0.6	331.14	1.20×10^{35}	0.9952	407.49	1.20×10^{35}	0.9963
0.7	315.30	1.44×10^{35}	0.9969	420.96	1.44×10^{35}	0.9988
0.8	323.31	1.37×10^{23}	0.9970	325.49	1.37×10^{23}	0.9989
0.9	326.95	2.59×10^{24}	0.9982	374.48	2.59×10^{24}	0.9997

The existence of multisteps in the thermal degradation curves of nanocomposites indicates: (1) the thermal stability of CS in the nanocomposites depends on the interactions of CS with Z [17-21], and (2) the thermal degradation of CS in the nanocomposites follows a complex reaction path (Table 2).

The activation energy *E*a of the chitosan-zeolite composite increases up to a conversion degree of α = 0.7 after which it remains relatively constant. A similar trend is observed for the pre-exponential factor A.

CONCLUSIONS

Differential thermogravimetric and thermal analysis (TGA/DTA) experiments were carried out to compare the thermal stability of the samples studied, and to determine the kinetic parameters involved in their degradation process, such as the activation energy (*E*a) of degradation, the frequency factor (*A*), and the degradation mechanism, known as *the kinetics triplet*.

The studies performed and the results obtained give us sufficient information about the thermal properties of CSZ composite and its stability. Its properties such as hydrophilicity, biocompatibility, biodegradability, antibacteriality, non-toxicity and adsorptivity make it an excellent material in the preparation of medical products. The kinetic properties determined during its thermal decomposition can be used in the development of technologies for its processing. The studies carried out can be used in the preparation of bandage materials with defined properties.

It was established that this kinetics model could be used for a quantitative description of the non-isothermal decomposition process of samples, which corresponds to a random scission mechanism.

REFERENCES

1. S. Olivera, H. B. Muralidhara, K. Venkatesh, V. K. Guna, K. Gopalakrishna, K. Yogesh, Kumar, *Carbohydr. Polym.*, **153**, 600 (2016). DOI: 10.1016/j.carbpol.2016.08.017
2. M. Vakili, M. Rafatullah, B. Salamatinia, A. Z. Abdullah, M. H. Ibrahim, K. B. Tan, Z. Gholami, P. Amouzgar, *Carbohydr. Polym.*, **113**, 115 (2014). DOI: https://doi.org/10.1016/j.carbpol.2014.07.007
3. H. Moussout, H. Ahlafi, M. Aazza, C. El Akili, *Int. J. Biol. Macromol.*, **108**, 1063 (2018). DOI: https://doi.org/10.1016/j.ijbiomac.2017.11.018
4. H. Moussout, H. Ahlafi, M. Aazza, O. Zegaoui, C. El Akili, *Water Sci. Technol.*, **73 (**9), 1199 (2016). DOI: 10.2166/wst.2016.075
5. H. Moussout, H. Ahlafi, M. Aazza, C. Sekkate, *Cellulose*, **25**, 5593 (2018). DOI:10.1007/s10570-018-1999-5
6. A. Anitha, S. Sowmya, P. T.S. Kumar, S. Deepthi, K. P. Chennazhi, H. Ehrlich, H. Ehrlich, M. Tsurkan, R. Jayakumar, *Prog. Polym. Sci.,* **39**, 1644 (2014). DOI: https://doi.org/10.1016/j.progpolymsci.2014.02.008
7. E. Khor, L. Y. Lim, *Biomaterials*, **24**, 2339 (2003). DOI: https://doi.org/10.1016/S0142-9612(03)00026-7
8. V. K. Thakur, S. I. Voicu, *Carbohydr. Polym.*, **146**, 148 (2016). DOI: 10.1016/j.carbpol.2016.03.030

9. P. Gogoi, A., Thakur, R. R. Devi, B. Das, T. K. Maji, *J. Environ. Chem. Eng*., **4**, 4248 (2016). DOI:10.1016/j.jece.2016.09.027
10. S. Noori, M. Kokabi, Z.M. Hassan, *Procedia Mater. Sci*., **11**, 152 (2015) DOI:10.1016/j.mspro.2015.11.023
11. H. Moussout, H. Ahlafi, M. Aazza, A. Amechrouq, *Thermochim. Acta*, **668**, 169 (2018). DOI: https://doi.org/10.1016/j.tca.2018.08.023
12. A. Ali, S. Ahmed, *Int. J. Biol. Macromol*., **109**, 273 (2018). DOI: https://doi.org/10.1016/j.ijbiomac.2017.12.078
13. E. M. S. Azzam, G. Eshaq, A. M. Rabie, A. A. Bakr, A. A. Abd-Elaal, A. E. El Metwally, S. M. Tawfik, *Int. J. Biol. Macromol*., **89**, 507 (2016). DOI: 10.1016/j.ijbiomac.2016.05.004
14. D. T. Zvezdova, N. M. Nedelchev, *Science & Technologies, Technical studies,* **II** (4), 15-(2012)
15. D. T. Zvezdova, *J. Therm. Anal. Calorim*., **149** (14), 7355 (2024). DOI:10.1007/s10973-024-13338-7
16. T. Ozawa, *Bull. Chem. Soc. Jpn*., **38**, 1881 (1965). DOI:10.1007/s10973-012-2882-5
17. I. Corazzari, R. Nistico, F. Turci, M. G. Faga, F. Franzoso, S. Tabasso, G. Magnacca, *Polym. Degrad. Stab*., **112**, 1 (2015). DOI:10.1016/j.polymdegradstab.2014.12.006
18. C.-Y. Ou, C. H. Zhang, S. D. Li, L. Yang, J.-J. Dong, X. L. Mo, M. Zeng, *Carbohydr. Polym*., **82**, 1284 (2010). DOI: https://doi.org/10.1016/j.carbpol.2010.07.010
19. M. R. Ricciardi, V. Antonucci, M. Giordano, M. Zarrelli, *J. Fire Sci*., **30**, 318 (2012). DOI:10.1177/0734904112439293
20. S. Sinha Ray, *Env. Friendly Polym. Nanocomp*., 295 (2013). DOI:10.1533/9780857097828.2.295