Thermo-oxidative degradation of chitin and chitosan derived from dead bees

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Abstract. This study investigates the thermo-oxidative degradation of chitin and chitosan extracted from dead bees using thermal analysis methods. The research reveals both similarities and unique characteristics in the thermal decomposition of these polysaccharides, along with a comparative assessment of their thermal stability. Utilizing thermogravimetry, derivative thermogravimetry, and differential scanning calorimetry techniques, the study identifies three distinct stages of thermal decomposition for both biopolymers: water desorption, active pyrolysis, and final decomposition with residual carbon formation. The findings demonstrate that chitin exhibits higher thermal stability compared to chitosan, likely due to its acetylated structure. Chitin undergoes desorption of both free and bound water molecules, while chitosan only loses free water. The study provides valuable insights into the thermal behavior of these biopolymers derived from dead bees, which is crucial for their application in various fields such as biomedicine, agriculture, and materials science. The use of dead bees as a raw material presents a cost-effective alternative to traditional sources like crustacean shells for producing chitin and chitosan.

1 Introduction

Due to the steady increase in practical applications across various spheres of human activity, special attention has been given in recent years to unique aminopolysaccharides such as chitin and its deacetylated derivative, chitosan. The study of these biopolymers has evolved into a distinct branch of science known as "chitinology" [1].

Crustacean shells have traditionally served as the primary natural source of raw materials for chitin and chitosan production in many countries. However, despite the existence of over a dozen developed methods for extracting chitin from crustacean shells, authors in several studies note that these shells remain a relatively expensive raw material [2]. Consequently, there is a need to explore potential alternative sources for obtaining chitin and chitosan. These alternatives may include small crustaceans, insects, silkworms, house flies, dead bees, and others.

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2 Materials and methods

In this study, chitin and chitosan obtained from local natural raw materials – dead bees - were investigated.

The raw material from dead bees was preliminarily dried at 35°C and ground. The biomass was then subjected to demineralization with 2M hydrochloric acid at room temperature for 5 hours. Subsequently, deproteinization of the biomass was carried out by treating the raw material with a 1N NaOH solution. Chitosan was obtained by deacetylation of the resulting chitin with a 50% aqueous sodium hydroxide solution at a temperature of 120°C for 4 hours.

Thermal analysis was performed on a LINSEIS STA PT1600 synchronous thermal analyzer (Germany) using thermogravimetry (TG), derivative thermogravimetry (DTG), and differential scanning calorimetry (DSC) methods. Measurements were conducted in an air atmosphere in dynamic mode with a heating rate of 10 degrees per minute in the temperature range from 27.0 to 800°C. The initial mass of the samples was 14.4 mg. When performing thermal analysis of the studied samples, the recommendations indicated in works [3-5] were followed. Subsequent processing of the obtained experimental data was carried out using the instrument's software package.

In the present study, chitin and chitosan derived from local natural raw material – dead bees - were investigated.

3 Results and discussion

3.1 Chitin

The comprehensive analysis of thermograms (TG, DTG, DSC) in Figures 1 and 2, and Table 1 allows for the identification of three consecutive stages of thermal decomposition of chitin and chitosan:

Water molecule desorption stage;

Active pyrolysis stage;

Final decomposition and coke residue formation stage.

The stage boundaries are marked with vertical dashed lines in the figure. Let us examine the chitin thermograms by stages.

The first stage (1) of mass changes is relatively low-temperature, covering the temperature range from 27.0 to 179.6°C, with $\Delta T_1 = 179.6 - 27.0 = 152.6$°C. A detailed joint analysis of the TG and DTG curves reveals that stage 1 of mass changes includes two parts: initial (1.1), relatively intense in the temperature range of 27.0 - 109.1°C; and final (1.2), with barely noticeable intensity (on the DTG curve) in the temperature range of 109.1 - 179.6°C.

During the first stage, sorbed water molecules are removed from the sample. The amount can be estimated from the TG curve, with a numerical value determined from the left mass change scale (Figure 1) as a percentage of the initial sample weight. It equals $\Delta m_1 = -6.1\%$. The negative sign indicates mass loss. Figure 1 and Table 1 show that the main portion of desorbed water ($\Delta m_{1.1} = -5.1\%$) occurs during the initial part of the first stage (1.1), when free water molecules are removed. The remaining bound water molecules ($\Delta m_{1.2} = -1.0\%$) are removed upon further heating of the polysaccharide.

The first stage of mass loss on the DTG curve is marked by a peak with a minimum (or so-called "inflection point") at 65.9°C, corresponding to the maximum instantaneous mass loss rate $V_{max1.1} = -1.65$ %/min in the initial part (1.1), and an almost imperceptible curve decrease with a minimum at 132.1°C in the final part (1.2).

The DSC curve in the first stage of mass changes is characterized by two endothermic effects (associated with the aforementioned desorption processes) with minima at 65.1 and 149.7°C, superimposed on a stronger exothermic effect at 126.4°C. The energy assessment of the endothermic effects is -296.83 and -48.86 kJ/kg, respectively.

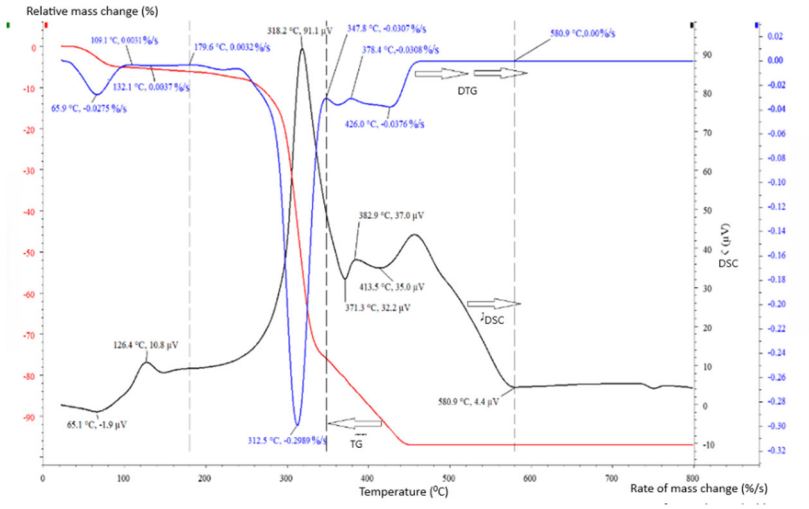

Fig. 1. Experimental curves of TG, DTG and DSC of chitin from dead bees.

The second stage (2) of mass changes is characterized as medium-temperature, ranging from 179.6 to 347.8 °C (ΔT_2 = 152.6 °C), and represents mass losses attributed to the thermo-oxidative degradation of chitin. According to the TG curve in Fig. 1, this mass change stage can be conditionally divided into two parts: an initial phase with moderate loss rates ($\Delta m_{2.1}$) in the temperature range of 179.6–293.0 °C, and a final phase with maximum mass loss rates in the narrow range of 293.0–347.8 °C. The mass losses $\Delta m_{2.1}$ and $\Delta m_{2.2}$ in these segments are -23.9% and -46.2%, respectively. Thus, the most significant mass losses are observed in the final part of stage 2 within a narrow temperature range of 54.8 °C. Notably, this segment exhibits the most prominent "inflection point" of the DTG curve at 312.5 °C, with an instantaneous maximum loss rate reaching V_{max} = -17.934 %/min (or -0.2989 %/s). It can be observed that at the DTG "inflection point," there is a sharp change in the course of the thermo-oxidative degradation reaction, where the uniformly accelerated nature of thermo-oxidative degradation up to 312.5 °C gives way to a uniformly decelerated process after the specified temperature. In support of this, the TG curve shows a breaking point with some delay at 331.7 °C, which serves as an intermediate point and delineates two linear segments of the TG curve (from 300.0 to 326.0 °C and from 337.1 to 440.0 °C).

The total mass loss value at the second stage is Δm_2 = -70.1%.

The processes of thermo-oxidative degradation of chitin at the second stage are marked on the DSC curve by a powerful exothermic effect with a maximum at 318.2°C. The energetic assessment of the effect is 2590 kJ/kg.

In this case, the extreme point of the DSC curve occupies an intermediate position between the "inflection point" on the DTG and the transition point on the TG. A similar sequence of extreme points on the thermograms (at somewhat lower temperature values of 252.3, 283.0, 309.6°C) is observed during temperature scanning of chitosan.

Table 1. Main characteristics of thermo-oxidative decomposition of chitin and chitosan.

Sample name	Stages	Temperature interval, ΔT, °C	Maximum loss rate temperature, T_{max}, °C	Maximum loss rate, V_{max}, %·min^{-1}	Changes in mass at this stage and (total), Δm, %	Coke residue, %
Chitin	1.1	27.0÷109.1	65.9	-1.65	-5.1 (-5.1)	
	1.2	109.1÷179.6	132.1	-0.222	-1.0 (-6.1)	
	2	179.6÷347.8	312.5	-17.93	-69.8 (-75.9)	
	3	347.8÷580.9	426.0	-2.40	-21.2 (-97.1)	2.9
Chitosan	1	27.0÷182.0	87.8	-1.434	-5.3 (-5.3)	
	2	182.0÷360.9	252.3	-7.998	-57.9 (-63.2)	1.3
	3	360.9÷609.3	523.0	-1.866	-35.5 (-98.7)	

The third stage (3) covers the temperature range ΔT_3 = 347.8 – 612.9 = 233.1°C. At this stage, the final part of the thermo-oxidative degradation process is observed (TG curve). On the DSC curve, exothermic effects with maxima at 382.9 and 456.3°C can be seen, which are likely due to the heterogeneous nature of thermo-oxidative decomposition and the formation of coke residue. Mass losses at this stage are estimated at Δm_3 = -20.9%. The mass of the coked residue is 2.9%.

3.2 Chitosan

Figure 2 presents the thermograms of chitosan. Although the mass changes in chitosan also occur in three stages, the thermal behavior observed in the curves differs somewhat from that of chitin. In the first stage, water desorption from chitosan occurs in a single step within the temperature range of 27.0 to 182 °C (ΔT_1 = 155.0 °C).

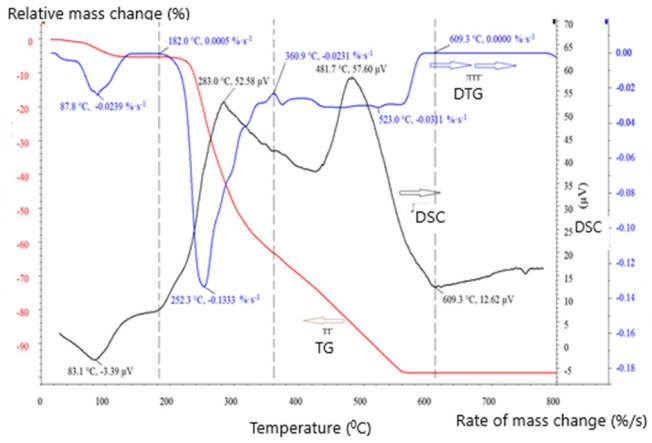

Fig. 2. Experimental curves of TG, DTG and DSC of chitosan from dead bees.

The maximum rate of free water molecule removal is V_{max1} = –1.434 %/min, recorded at a temperature of 87.8 °C, which is slightly higher compared to chitin. This indicates a relatively greater difficulty in desorption in this case, likely due to structural differences

between the compared polysaccharides. The mass loss during the first stage is $\Delta m_1 = -5.3\%$. Unlike chitin, no desorption of bound water molecules is observed in chitosan.

The DSC thermogram for this stage exhibits an endothermic effect with a minimum at 83.1 °C.

Generally, all plant polysaccharides, except for chitin and cellulose, are hydrated. Hydration is often observed in both crystalline regions and amorphous areas [6].

The second stage, characterized by active manifestation of thermo-oxidative degradation of chitosan, encompasses a temperature range from 182.0 to 360.9°C ($\Delta T_2 = 178.9$°C). The maximum rate of mass loss $V_{max} = -7.998$ %/min (or -0.1333 %/s) occurs at $T_{max} = 252.3$°C. The mass loss of chitosan at this stage amounts to $\Delta m_2 = -58.5\%$ of the initial mass.

The DSC curve of chitosan in the second stage exhibits an exothermic peak with a maximum at 283.0°C. Its intensity is 1.73 times lower than that of chitin.

The third stage of mass changes encompasses a range of $\Delta T_3 = 248.4$°C (from 360.9 to 609.3°C). The mass loss constitutes $\Delta m3 = -35.5\%$. The DSC curve at this stage demonstrates an exothermic effect with a maximum at 481.7°C.

Table 2. Values of characteristic temperatures at fixed values of mass loss (in %).

Samples	Characteristic temperatures, °C			
	T_{20}	T_{30}	T_{40}	T_{50}
Chitin	296.8	304.7	310.6	316.2
Chitosan	250.5	263.7	280.7	302.0

Table 2 presents numerical data of characteristic temperatures T_{20}, T_{30}, T_{40}, T_{50}, at which 20, 30, 40, 50% mass loss is observed under identical experimental conditions [7]. These data allow for a relative assessment of the thermal stability of the examined polysaccharide samples. The presented data demonstrate a higher thermal resistance of chitin compared to chitosan. This is a consequence of the chitin deacetylation process. The harsher the conditions of chitin deacetylation, the lower the thermal stability of the resulting chitosan [8-9].

In the study [10], comparative investigations of different chitin and chitosan samples were conducted using temperature-programmed desorption mass spectrometry. The contour of the pressure (p) versus temperature (T) curves for volatile products of chitin and chitosan thermolysis replicates the course of DTG curves (in an inverted form, being a mirror image) of these biopolymers in numerous other studies performed using thermal analysis methods. The degree of asymmetry in the $p = f(T)$ dependencies and DTG curves is also identical, manifesting in a clearly greater extension (on the temperature scale) of the low-temperature wing of chitin compared to the high-temperature wing. The opposite asymmetry pattern is observed for chitosan, where the low-temperature wing is much wider than the high-temperature wing. In our case, the aforementioned asymmetry of DTG peaks is also observed in the second stage of polymer decomposition. The authors of the study [10] attribute the observed asymmetry in the $p = f(T)$ dependence of chitin to the thermolysis of pyranose cycles containing free amino groups. In the case of chitosan, thermolysis is associated with the decomposition of pyranose cycles containing the acetamide group.

The authors of the study [11] reached the same conclusion, considering the differences in the chemical structure of polysaccharides (mainly, different content of amino and acetamide groups) and based on the analysis of experimental thermograms obtained by scanning in the temperature range of 40 - 850°C in a nitrogen atmosphere of chitin and chitosan samples isolated from shrimp and crab shells, respectively.

4 Conclusion

The thermal decomposition of chitin and chitosan occurs in three stages, with the boundaries and width of these stages being unique to each biopolymer.

During the programmed heating of chitin, desorption of both free and bound water molecules is observed, whereas in the case of chitosan, only free water molecules are desorbed.

The differences in the chemical structure of chitin and chitosan significantly influence the contours of the recorded experimental thermograms, particularly during the active pyrolysis stage.

The relative thermal stability of chitosan in the temperature range of 240-315°C is noticeably lower than that of chitin.

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