CHARACTERISATION OF CHITOSAN AND CHITOSAN-BASED MATERIALS BY TEMPERATURE PROGRAMMED DESORPTION MASS SPECTROMETRY

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Abstract

The thermal behaviour of chitin, chitosan, and their derivatives is of great importance both for practical applications and for understanding the processes of interaction with additional compounds comprising chitosan-based materials. In this work, the samples of chitin and chitosan obtained in our laboratory from various sources (insects, mushrooms) and commercial samples, as well as derivatives containing iodine, fucorcinum, methylene blue, neomycin, etc., were studied with temperature programmed desorption mass spectrometry. The method reveals the differences in the dehydration of samples. Thermal decomposition in the temperature range from 150 to 200°C is associated with decarboxylation, and above 200°C with decomposition of the main chain. The thermal behaviour of samples depends on the origin of chitin, i.e., the fungal chitin starts to decompose at a lower temperature than insect chitin. The latter one shows thermal behaviour comparable to that of chitin from crustaceans. Chitosan obtained from chitin of various origins is more uniform. The additives in the derivative materials influence the thermal behaviour in different ways, especially a substantial difference was seen in the case of iodine combined with fucorcinum.

Keywords: *temperature programmed desorption mass spectrometry, chitin, chitosan*

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1. Introduction

Chitin is a non-toxic, biodegradable polymer that is widespread in nature; it ranks second after cellulose. It is a main component of crustacean shells, forms the chitinous cover of insects, and is an ingredient of the cell walls of fungi. As a rule, commercial chitin is obtained from seafood waste in the food industry (crab, shrimp). Nevertheless, fungal chitin and chitin from industrially significant insects (for example, *Hermetia illucens*) are becoming increasingly important. One of the disadvantages of chitin is its low solubility in common solvents, which somewhat obstructs the processing of this polymer, particularly with respect to its cost, and therefore its applications. Despite this, chitin is used in various industries, for instance, for the production of biomaterials, due to the development of new, more cost-effective technologies [1].

Chitosan, chemically a cationic polysaccharide, is obtained from chitin by alkaline or enzymatic deacetylation - hydrolysis of acetamide groups in the C2 position of the chitin monomer. Chitin and chitosan are linear polysaccharides consisting of randomly distributed 2-acetamide-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose linked by a β-(1→4) glycosidic bond (Figure 1).

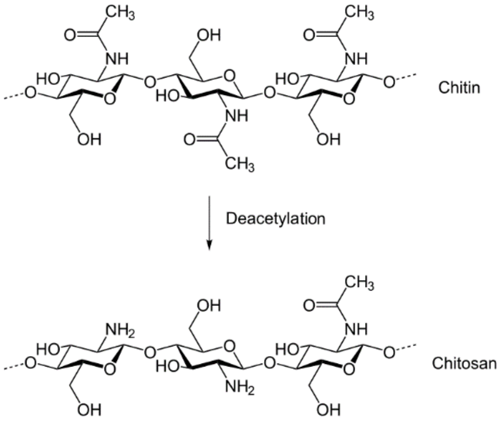


Figure 1. Conversion of chitin into chitosan by deacetylation.

An important parameter of chitin and chitosan is the degree of deacetylation, reflecting the percentage of aminoglucopyranose units. The degree of deacetylation (for chitin < 50%) affects these biopolymers' physical, chemical, and biological properties, including thermal behaviour. Chitosan is widely used in medicine, the food industry, cosmetology, etc. [2]. It is soluble in weak organic acids (in 1% acetic acid in particular) and can be relatively easily modified to obtain various derivatives. There are many works investigating the properties of chitosan in relation to its structure. Thermal behaviour was studied in relation to thermal degradation using thermogravimetry (TGA) and differential scanning calorimetry (DSC) [3]. The main range of thermal destruction of chitin is 300 - 400°C. The thermal stability of chitin depends on its origin, with the order of krill > shrimp > crab > squid, and on its crystalline characteristics, e.g., type of crystalline structure, size and perfection of crystallites [3]. Furthermore, the thermal behaviour of chitosan was also investigated using TG-FTIR and TG-GG MS to study the volatile compounds produced during degradation and dehydration. The effect of deacetylation degree on thermal processes using TG-FTIR is assessed in the literature [4]. Decomposition of chitosan with a higher degree of deacetylation occurs in two stages, whereas decomposition of chitin occurs mainly in one stage, but at higher temperatures. Thermogravimetry was used to determine physically and chemically bound water. The literature reports on the applicability of thermogravimetry for measuring the amount of chitin added to soil, as well as for detecting chitin by the peak pyrolysis rate (385°C); also for cellulose, chitosan, *N*-acetylglucosamine and *N*,*N'*-diacetylchitobiose at 340°C, 300°C, 200°C, and 240°C, respectively [5]. TGA and FTIR, together with other methods, were used to confirm the authenticity of mushroom chitosan [6]. Several works were dedicated to studying the kinetics and mechanisms of thermal degradation of chitin and chitosan [7–10].

Recently, chitin and chitosan have attracted interest as energy storage media and are used to produce nitrogen-doped porous carbon, specifically porous carbon fibres and nanofibrous microspheres with hierarchical porosity. The presence of nitrogen in the carbon network changes the wettability and polarity of its surface, as well as its electronic properties. This can trigger Faraday oxidation-reduction reactions with electrolyte ions, which are essential for electrochemical capacitors. The possibility of using chitin and chitosan to produce hard carbon for Na-ion batteries is also examined in the literature [11]. Catalysts based on nitrogen-doped carbon nanosheets can be obtained by pyrolysis of chitosan with melamine additives [12].

Chitin, similar to cellulose, can be considered an alternative source of renewable energy. In this regard, a lot of work has been devoted to the pyrolysis of chitin and chitosan [13]. For instance, it was reported that chitosan decomposes and carbonises at 252°C [14]. The composition of the volatile products included pyrazines, pyridines, pyrroles, and furans. It was concluded that chitosan is a potential biomass source for obtaining nitrogen-containing aromatic heterocycles. Chitin of the insect *Hermetia illucens* can be a source of biochar enriched with nitrogen, stimulating plants and soil crustaceans [15]. Also, crab shells have a high potential as a precursor of nitrogen-containing biochar [16]. Knowledge of the thermal characteristics of biopolymers is also indispensable for the development and production of biodegradable thermoplastics [17, 18].

Several works present data on the TG characteristics of chitosan derivatives, particularly chitosan-*N*-phenylacetamide [19]. Bajer *et al.* [20] investigated the thermal characteristics of chitosan modified with heterocyclic dyes. Podust *et al.* [21] presented the TG/DTG and temperature programmed desorption mass spectrometry (TPDMS) characteristics of hybrid chitosan/nanosilica materials.

There is little information in the literature specifically on TPDMS of chitin and chitosan. Therefore, the purpose of this work is to analyse and summarise the results of TPDMS studies of chitin and chitosan samples obtained from various sources, as well as iodine-containing chitosan derivatives. Thermogravimetry was mainly used to characterise chitin and chitosan samples, as well as their derivatives and materials obtained from them.

2. Materials and Methods

2.1. Chitin, Chitosan, Chitosan Derivatives

In this work, commercial chitin samples without additional purification, as well as samples of chitin and chitosan obtained in the laboratory from mushrooms and insects, were used (Table 1).

Table 1. Chitin and chitosan obtained from various sources.

Sample source	Chitin yield [%]	Chitosan yield [%]
Hericium erinaceus	5.54	0.44
Ganoderma lucidum	10.70	0.73
Ophiocordyceps sinensis	3.55	1.75
Blattella germanica	11.00	5.77
Hermetia illucens imago	9.01	1.10
Hermetia illucens exuviae	50.61	41.26
Hermetia illucens puparia	66.25	31.90
Crab chitin	-	-

To obtain chitin from insects and mushrooms, a procedure of short-term (1 h) treatment with 1 M hydrochloric acid and subsequent 1 M alkali treatment for 24 h at room temperature was applied. Hydrogen peroxide was used for bleaching. The obtained chitin was deacetylated using 30 - 50% alkali at room temperature for 72 h or for 1 h at 80°C. Samples were washed with water and used for further studies. Chitosan iodides were obtained using an original method [22], using chitosan and concentrated HI. Chitosan iodide is formed according to the following reaction:

$$(\text{Chitosan-NH}_2)_n + n\ \text{HI} \rightarrow (\text{Chitosan-NH}_3\text{I})_n. \quad (1)$$

The procedures of obtaining chitosan derivatives were similar to those described previously [23]. In the case of the fucorcinum-containing derivative, 2 g of chitosan was added to 50 ml of distilled water and left to activate for 1 h. Concentrated HI was added dropwise with vigorous stirring for 20 min until chitosan was dissolved. Fucorcinum solution was introduced, and the solution was stirred actively for 10 min. To obtain chitosan iodide with methylene blue, 1 g of chitosan was added to 30 ml of distilled water and left for 1 h. Concentrated HI was added dropwise until chitosan was dissolved and the pH was 4.0, and the mixture was actively mixed. 0.04 g of methylene blue was dissolved separately in 20 ml of warm water (50 - 60°C). Two solutions were combined (total volume 50 ml) and stirred for the next 10 min. Sponges based on chitosan iodide with additional components (dyes, antibiotics, etc.) were obtained by lyophilisation of the initial solutions. To obtain porous materials, wet (not dried completely) substances were freeze-dried for 48 h under a 10^{-2} Pa pressure using a homemade glass vacuum system with liquid nitrogen.

2.2. Temperature Programmed Desorption Mass Spectrometry

The samples were analysed using a temperature programmed desorption mass spectrometry setup consisting of a programmable vacuum oven and an MX7304 mass spectrometer (electron impact ionisation of gaseous samples). Linear heating of the samples was performed from room temperature to 900°C with simultaneous mass spectrometric analysis of gas-phase products (mass spectra were recorded in the mass range from 1 to 200 Da).

3. Results and Discussion

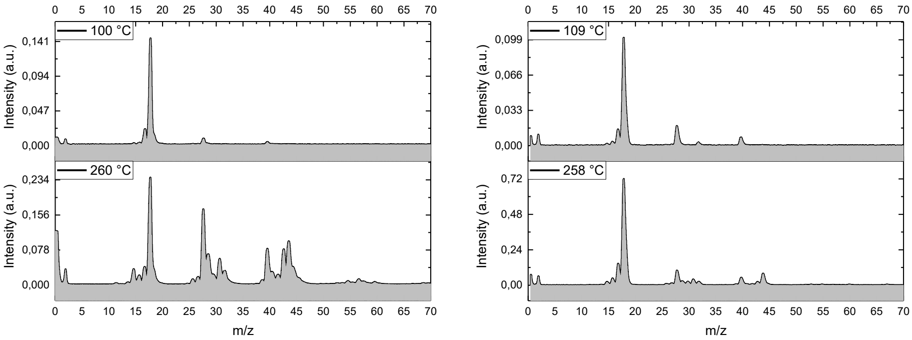
When chitin and chitosan are heated from 30 to 100°C, physically adsorbed water evaporates (polysaccharides are highly hygroscopic). Weight loss at this stage is usually ca. 10%. Weight loss when heated from 200 to 400°C results from decomposition, depolymerisation, and formation of char. Chitin and chitosan decompose in a similar temperature range; however, different kinetics are observed. Chitin decomposes in one stage at 360°C with the simultaneous release of relatively large amounts of CO and H_2O, less CO_2, H_2, NO, and O_2. The deacetylated analogue of chitosan requires two stages of conversion into char. Its TPDMS spectrum is mainly dominated by a broad peak of H_2O (280°C). In addition to physically adsorbed water, this may be water formed as a result of the reaction of two adjacent OH groups or as a result of the dehydration of two adjacent carboxyl groups. Desorption of other gases begins at approximately 240°C with the release of CO, NO and O_2. The decomposition process reaches its maximum at approximately 300°C, when CO_2, H_2, H_2O and N_2 are simultaneously desorbed from the surface of partially dehydrated and deaminated chitosan, and continues up to 400 - 500°C. The final modification of coal occurs at 500 - 850°C [11].

As a result of the studies conducted, mass spectra of various samples of chitin and chitosan were obtained. At 100°C, ions of m/z 2, ~~16,~~ 17, 18, 28, and 40 are detected in all mass spectra, which can be attributed to H_2, OH, NH_3, H_2O, CO and CN_2 (C_2O). At 300°C, in addition to the indicated ions, m/z 25 (C_2H), 26 (CN), 27 (CHN), 29 (HN_2), 30 (NO or H_2N_2), 38 (C_2N), 39 (C_2HN), 41 (CHN_2, acetonitrile C_2H_3N), 42 (N_3), 43 (HN_3), 44, 53, 55, 57, 59 (acetamide) ions are present. Ion of m/z 44 results from CO_2; other peaks correspond to the fragments of chitosan molecules. Ions of m/z 53, 55, 57, and 59 are not present in the mass spectra of commercial chitin (possibly due to a sufficiently high degree of purification). The mass spectra of chitin and chitosan did not differ in ionic composition. The main ionic species released at TPDMS analysis are shown in Table 2.

Table 2. Main ionic species released at TPDMS analysis.

Ion species	**m/z**
H_2O	18
HO, NH_3	17
CO_2	44
CO	28
O, NH_2, CH_4	16
CH_3COOH	60
NH, CH_3	15
Acetic acid decomposition	43
Acetic anhydride, C_2H_2O ($C_2H_4N^+$)	42
Acetaldehyde (CHO)	29
HCl	38, 37, 36, 35
HCN	27, 26
HNO, CH_3O	31
CHN_2, C_2H_3N	41

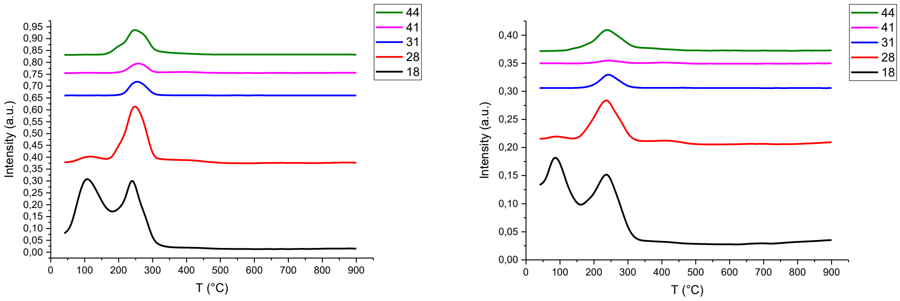
The most interesting ions are those of m/z 18 (H_2O), 28 (CO), 44 (CO_2) and 41, since the temperature profiles of the release of these ions have certain differences. Typical mass spectra of gaseous products of chitin-based materials thermal decomposition at temperatures of 100°C and 260°C are presented in Figure 2. The spectra of *Hericium erinaceus* chitin-based materials are shown as an example of the mushroom species.



(a) **(b)**

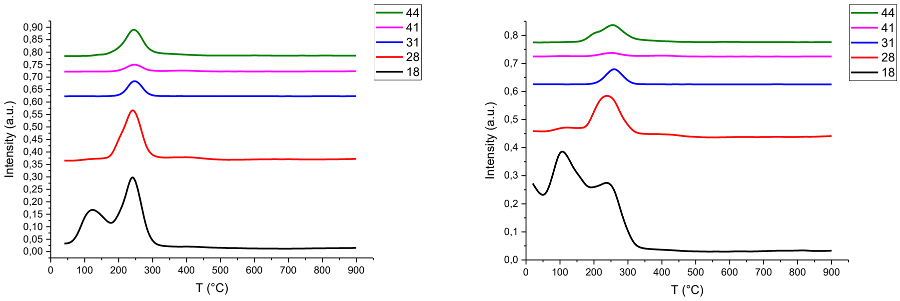
Figure 2. Typical mass spectra of gaseous products of chitin-based materials thermal decomposition at temperatures of 100°C and 260°C: (a) mushroom species, (b) crustacean species giving much fewer products.

Temperature profiles of the gaseous product release (thermograms) of chitin and chitosan samples isolated from mushrooms and insects are shown in Figures 3–8.



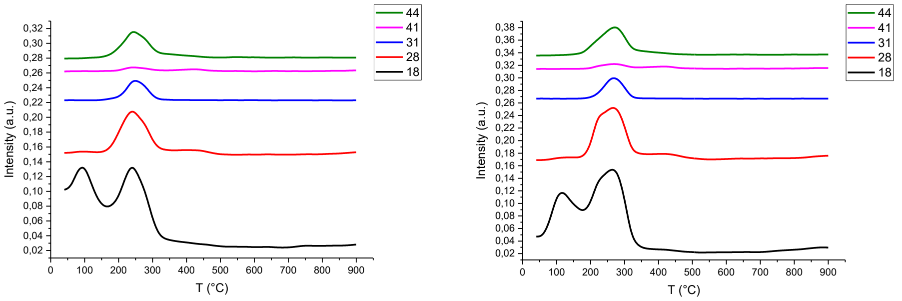
(a) **(b)**

Figure 3. Temperature profiles of gaseous species released from *Ganoderma lucidum* (a) chitin and (b) chitosan (legend refers to m/z of ions).



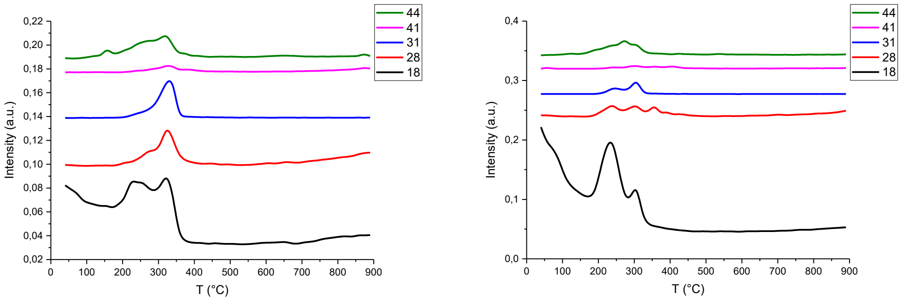
(a) **(b)**

Figure 4. Temperature profiles of gaseous species released from *Hericium erinaceus* (a) chitin and (b) chitosan (legend refers to m/z of ions).



(a) **(b)**

Figure 5. Temperature profiles of gaseous species released from *Ophiocordyceps sinensis* (a) chitin and (b) chitosan (legend refers to m/z of ions).

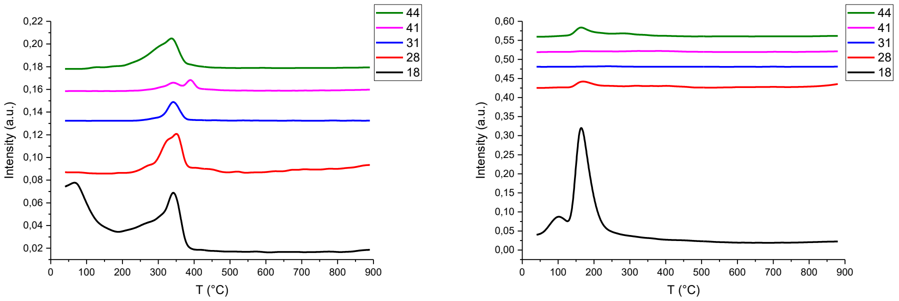


(a) **(b)**

Figure 6. Temperature profiles of gaseous species released from *Blattella germanica* (a) chitin and (b) chitosan (legend refers to m/z of ions).

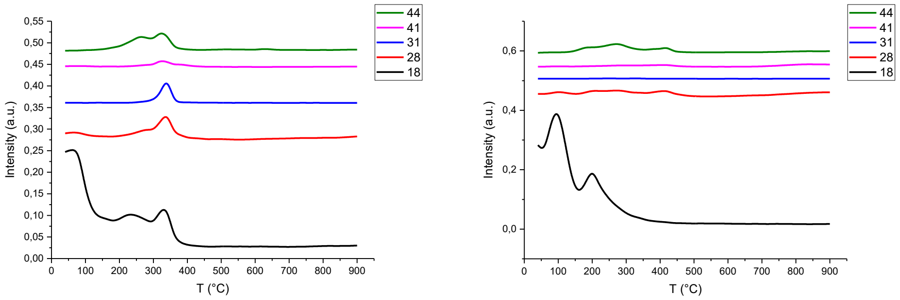
The gaseous species release profiles in TPDMS analysis of chitin from different mushrooms and chitosan obtained from them are very similar. They are all characterised by two maxima of water release: about 100°C (adsorbed water, ‘final drying’ of the sample) and a maximum at 200°C (the evaporation of more strongly bound water, apparently the hydrates). The maximum release of the gaseous products yielding ions of m/z 44 (CO_2), 28 (CO), 31 (HNO), and 41 (acetonitrile) is also observed at low temperatures of about 250°C. The ion of m/z 41 has a second high-temperature maximum at 400°C.

A completely different behaviour was noticed for the chitin isolated from insects (Figures 7a and 8a) and chitosan obtained from them. In addition to the two maxima of the release of bound water at 100 and 200°C, a third maximum appears at a higher temperature of ca. 300°C, indicating the presence of a third site of water bound to insect chitin. In parallel with this maximum, ions referring to m/z 44 (CO_2), 28 (CO), 31 (HNO) and 41 (acetonitrile) are also released at 300°C. The second maximum of the m/z 41 ion release is also present, but it is not shifted to higher temperatures, and as in the case of mushrooms, it is present at 400°C. In the case of chitosan obtained from these chitins (Figures 7b and 8b), the temperature profiles of gaseous species released differ in relation to the source chitin. The maximum of the water release at 300°C disappears, and the evacuation maxima of the ions of m/z 44 (CO_2), 28 (CO), 31 (HNO) and 41 shift to 200°C.



(a) **(b)**

Figure 7. Temperature profiles of gaseous species released from *Hermetia illucens* imago (a) chitin and (b) chitosan (legend refers to m/z of ions).



(a) **(b)**

Figure 8. Temperature profiles of gaseous species released from *Hermetia illucens* puparia (a) chitin and (b) chitosan (legend refers to m/z of ions).

In addition, in the insect-derived samples, several high-temperature maxima of the CO_2 release are observed (especially pronounced in the samples of *Hermetia illucens* puparia). Such maxima are characteristic of TPDMS analysis of crustacean chitin (Figure 9).

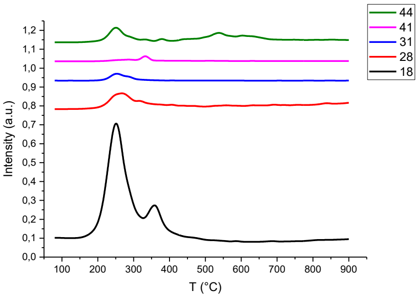
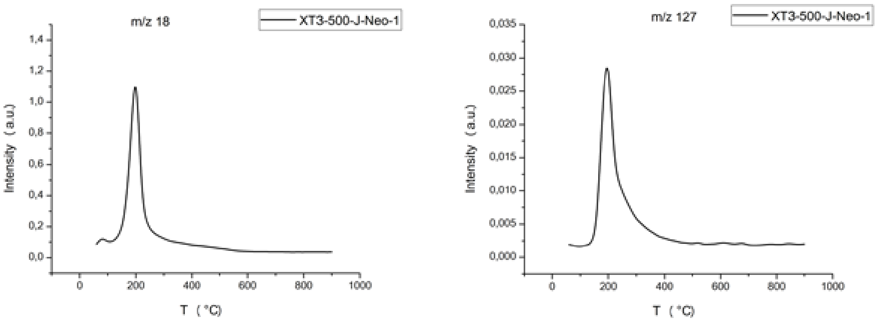


Figure 9. Temperature profiles of gaseous species released from commercial crab chitin (legend refers to m/z of ions).

3.1. Iodine-containing Derivatives

TPDMS analysis of selected chitosan-based materials containing iodine and various biologically active substances (Figures 10–13) was also performed. It was noticed that some of these substances significantly changed the thermal behaviour of the polymer.



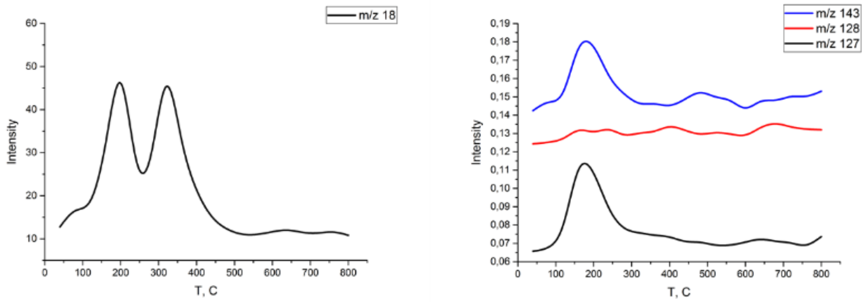
(a) **(b)**

Figure 10. The temperature profile of the release of (a) water (m/z 18) and (b) iodine (m/z 127) ions from the chitosan-iodine samples containing neomycin.

The release of water and iodine-containing ions is analogous for all tested samples with neomycin. Water is released at 200°C. In all samples, one maximum yield of iodine is detected at 200°C. In the mass spectra, in addition to the ion of m/z 127 ($[I]^+$), the m/z 128 ($[IH]^+$) ion was recorded, the yield profile of which coincides with that of the m/z 127 ions.

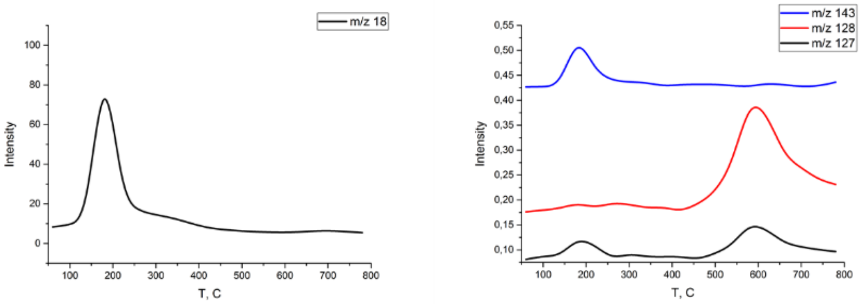
The thermograms of the samples containing fucorcinum and those without fucorcinum indicate differences in their nature in the context of the release of water and iodine-containing ions (Figures 11 and 12). In samples containing fucorcinum (Figure 12), one peak of water release is observed at about 200°C. In contrast, in the sample without fucorcinum (Figure 11), water is released at 200 and 350°C, i.e., the sample contains bound water. At the same time, in the sample without fucorcinum, iodine is released at 200°C, and m/z 127 ($[I]^+$) and 143 ($[IO]^+$) ions are observed in the mass spectra. The ion of m/z 143 was reported earlier in the mass spectra of pure chitosan on silica and was ascribed to the fragment ion of the carbohydrate monomers of chitosan [24]. In previous studies, however, these ions were accompanied by other fragments of m/z 145, 131, etc., which were not observed in the present research. Moreover, the ion of m/z 143 was observed by us only in the species containing iodine and accompanied by the m/z 127 ion, which allows identifying its stoichiometry as $[IO]^+$. In samples containing fucorcinum, there is a second, high-temperature maximum of iodine yield at 600°C. In this case, 128 ($[IH]^+$) and 143 ($[IO]^+$) ions are present in the mass spectra, which indicates that iodine in samples containing fucorcinum is differently bound, and its way of thermal decomposition differs significantly. This significant difference in the chemical structure of the samples requires further research.

In the chitosan samples containing methylene blue (Figure 13), water is released at 200 and 300°C, which indicates that water exists in two forms, bound differently to the polymeric matrix. Moreover, one maximum yield of iodine is detected at 200°C. Ions of m/z 127 ($[I]^+$) and 143 ($[IO]^+$) were recorded. The higher signal intensity of these ions was observed in the sample with higher methylene blue content.



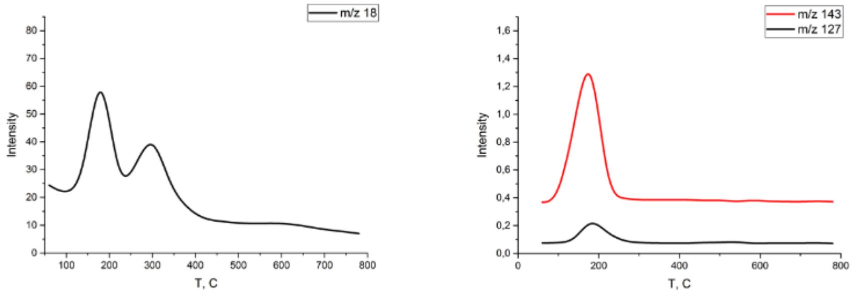
(a) **(b)**

Figure 11. The temperature profile of the release of (a) water (m/z 18) and (b) iodine-containing gaseous (m/z 127 ([I]$^+$), 128 ([IH]$^+$) and 143 ([IO]$^+$)) ions from the chitosan iodide without fucorcinum.



(a) **(b)**

Figure 12. The temperature profile of the release of (a) water (m/z 18) and (b) iodine-containing gaseous species (m/z 127 ([I]$^+$), 128 ([IH]$^+$) and 143 ([IO]$^+$)) from the chitosan iodide with fucorcinum.



(a) **(b)**

Figure 13. The temperature profile of the release of (a) water (m/z 18) and iodine-containing gaseous species (m/z 127 ([I]$^+$) and 143([IO]$^+$)) from the chitosan iodide with methylene blue.

4. Conclusions

The studies show that TPDMS analysis of chitin and chitosan from various sources and with different additives and modifiers can provide information on the binding of water to these materials and, in the case of iodine-containing chitosan derivatives, also on iodine binding. The effect of additives on this binding was also shown. The obtained data can be beneficial in understanding the processes of pyrolysis of chitinous materials, which can be crucial in obtaining so-called biochar and carbonaceous materials, such as catalysts and thermoplastics, from chitin and chitosan from various sources.

5. Acknowledgements

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