PHYSICOCHEMICAL PROPERTIES OF CHITIN ISOLATED FROM SHELL OF INDUSTRIAL CRABS OF VARIOUS SPECIES

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Abstract
Differential thermal analysis was carried out over the range of –190 ÷ 400 °C on six samples of chitin from shells of industrial crabs of various species. All samples of the chitin have several relaxation transitions of endothermal character (g_1-, g_2-, β- and γ-).

Key words: *chitin, physicochemical properties, shell, industrial crabs of various species.*

1. Introduction

Recycling of waste products from crab processing plants has an important ecological impact. Chitin obtained from the shells requires additional processing to reduce its molecular weight. This reduction can be achieved by using microorganisms. It is important to investigate the physicochemical characteristics, particularly the temperatures of physical transitions of chitin and its derivative chitosan, and their differences between various species of crabs in order to understand mechanisms of chitin/chitosan microbial destruction. Therefore differential thermal analysis (DTA) was carried out over the range of –190 ÷ 400 °C on six samples of chitin produced in Russian Federal Research Institute of Fisheries and Oceanography (Moscow, RUSSIA) from shells of industrial crabs of various species.

2. Materials and methods

Six samples of chitin that were isolated from various species of crabs such as golden king crab (*Lithodes aequispinus*) (No 1), snow crab (*Chionoecetes opilio*) (No 2), Korean hair crab (*Erimacrus isenbeckii*) (No 3), blue king crab (*Paralithodes platypus*) (No 4), red king crab (*Paralithodes camtchaticus*) (No 5), tanner crab (*Chionoecetes bairdi*) (No 6) were studied. These crabs were caught at the intermolting stage in the Sea of Okhotsk during one season. The samples were demineralized. The separation of a protein component of the shell (deproteination) was carried out with 5% solution of NaOH at 20 - 22 °C during 24 h. Then the chitin was washed with distilled water till neutral pH of washing waters. Pigments – carothenoids (astoxanthine, xanthoxanthine – remained in the samples.

Our experiments showed that air-dried samples of the chitin contained from 8.3 to 11.8 mass.% water that evaporated from them at 120 - 127 °C as shown by the data from DTA (***Table 1, Figure 1***).

As a method of research works, the differential thermal analysis was used [1 - 3]. Runs over the range of –190 to 400 °C were conducted in a helium atmosphere using a device developed in the Laboratory of Thermochemistry at the Research Institute of Chemistry Nizhny Novgorod State University [4]. Quartz served as standard. The mass of a sample

Table 1. *Physicochemical properties and mean temperatures of physical transitions in chitin isolated from shell of crab of various species.*

Sample	No 1	No 2	No 3	No 4	No 5	No 6
Sample mass, g	0.1870	0.2054	0.1861	0.2330	0.2580	0.2558
Content of H_2O, mass%	9.0	9.0	11.8	8.5	10.4	8.3
$t_{vap}(H_2O)$, °C	120.5	124	122.5	127	123	127
t_γ, °C	-----	-----	0.5	-----	–22	–33
t_β, °C	22	19	30	-----	33	63
t_{g1}, °C	103	102.5	107	106.5	85	124
t_{g2}, °C	212	213	209	-----	262	206
t_{dest1}, °C	294	287	300.5	283.5	299.5	262
t_{dest2}, °C	326	324	325.5	326	325	326

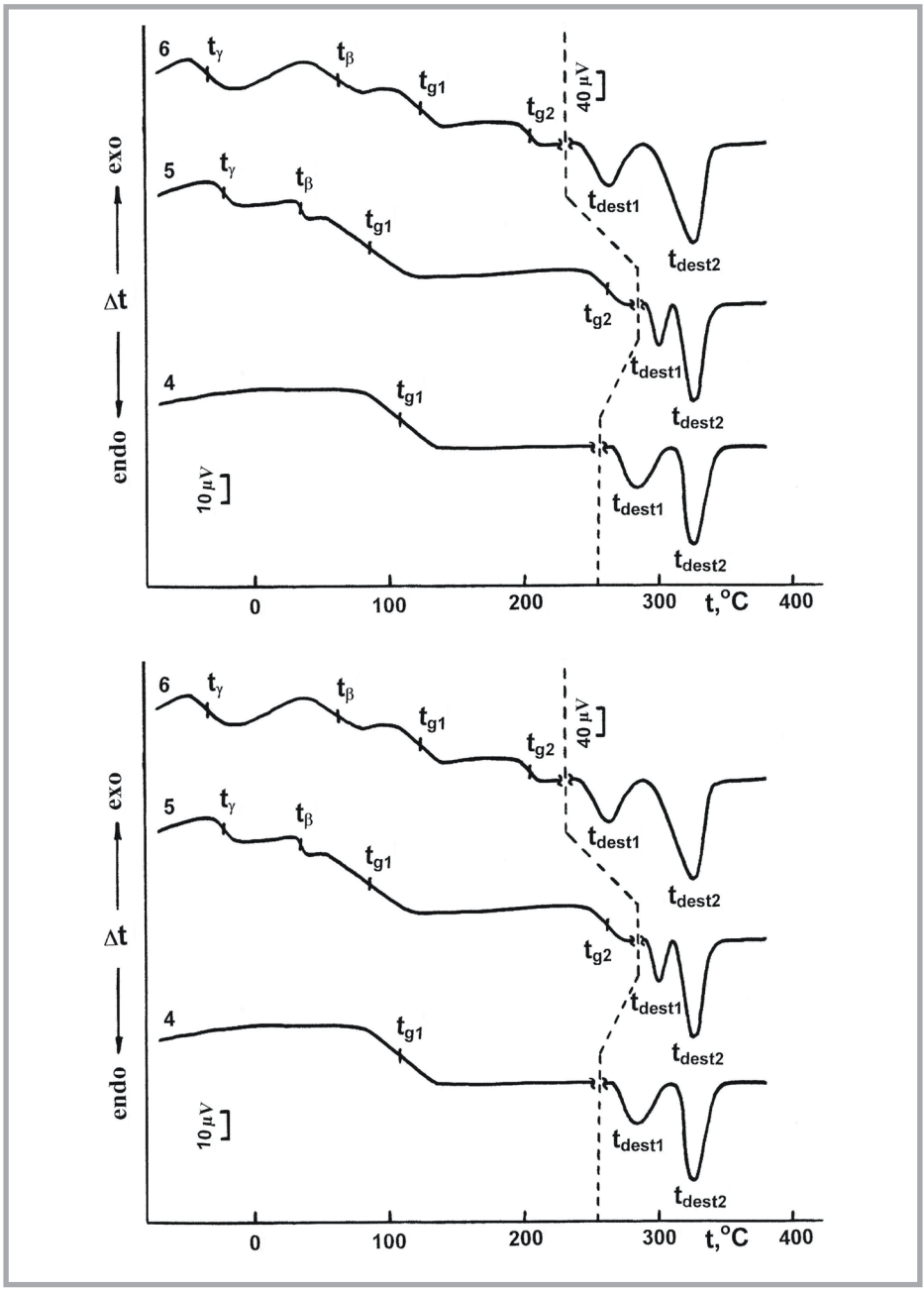

Figure 1. *Thermograms of dried chitin that were isolated from various species of crabs: 1 – golden king crab (Lithodes aequispinus); 2 – snow crab (Chionoecetes opilio); 3 – Korean hair crab (Erimacrus isenbeckii), 4 – blue king crab (Paralithodes platypus); 5 – red king crab (Paralithodes camtchaticus);6 – tanner crab (Chionoecetes bairdi).*

and of the standard was ~ 0.25 - 0.35 g. The temperature of the sample and the difference in temperatures between the sample and the standard were measured with a chromel-copel thermocouple to within ± 0.5°. The rate of heating in experiments was 5 °/min and the deviation from linearity did not exceed 1%. To check the DTA device operation the melting temperature (t_m) of standard n-heptane and the glass transition temperature (t_g) of purified glycerin were determined. The results obtained by us coincided with the corresponding reliable literature data for n-heptane [5] with an uncertainty of 0.2 °C and glycerin 1 °C [6].

The thermal chamber with the sample and standard was cooled with liquid nitrogen to –190 °C at a rate of ~20 °/min. Then it was heated at a rate of 5 °/min up to ~140 °C (the first warming-up) to record the endothermal peak of evaporation of sorbed water (***Table 1***). The heating was ended, the sample was cooled at a rate of 5 °/min down to room temperature, and simultaneously the evaporated sorbed water was pumped out *in situ* in the thermal chamber. Then the crucible with the sample was taken out from the thermal chamber, weighed on an analytical balance and the quantity of water contained in an air-dried sample was determined. Afterwards the sample was placed in an desiccator over $CaCl_2$. The next day the dried sample was placed in the thermal chamber and the experiment was repeated with heating the sample up to 380 °C (***Figure 1***).

3. Results and discussion

Figure 1 is examples demonstrating typical thermograms for samples No 1 - 6 of dried chitin that were isolated from various species of crabs. The averaged results and some physicochemical characteristics of the samples tested are given in ***Table 1***.

As seen from the thermograms, all the samples of chitin have several relaxation transitions of endothermal character (g_1-, g_2-, β- and γ-). Such processes were observed in earlier studies of samples of chitin isolated from various sources [7 - 10] as well as other polysaccharides [11 - 16].

According to the accepted classification [17 - 19] the γ-type transition appearing at a temperature below 0 °C (***Table 1, Figure 1***), is related to the excitation of vibrations of side branches of a polymer chain. It is suggested that those are present in macromolecules of the tested chitin. A similar pattern was observed by us for branched amylopectin [9, 14] and samples of hydrolyzed crab chitin and chitosan [10]. The β-type transition is caused by the excitation of vibrations of polymer chain segments that are smaller than a kinetic segment [17 - 19]. In cellulose, for example, an analogous process is explained as the excitation of vibrations of pyranose rings around a glucoside bond [20]. Two temperature intervals of devitrification (t_{g1} and t_{g2}) point to the availability of microregions of different degree of ordering (highly- and poorly ordered) in the examined chitin. The temperature of the first glass transition (t_{g1}) concerns the process in amorphous microregions. The temperature of the second glass transition (t_{g2}) is attributed to highly ordered microregions of the polymer.

Chitin derived from blue king crab (*Paralithodes platypus*) shell (No 4) showed unusual properties and its behavior was different from the rest of the samples analyzed. It

exhibited a single devitrification temperature (t_{g1} = 106.5 °C) and did not exhibit a γ- or a β- transition (***Table 1, Figure 1***, curve 4).

The γ-transition was observed in three samples (No 3, 5 and 6) with the highest, t_γ=0.5 °C, in sample No 3 (Korean hair crab, *Erimacrus isenbeckii*), and the lowest, t_γ= –33 °C, in sample No 6 (tanner crab, *Chionoecetes bairdi*).

All samples except No 4 registered a β-transition. The highest, t_β = 63 °C , was recorded for sample No 6 (tanner crab, *Chionoecetes bairdi*), and the lowest, t_β = 19 °C , for sample No 2 (snow crab, *Chionoecetes opilio*).

Vitrification temperatures were not significantly different between the analyzed chitin samples ($t_{g1} \approx 110$ °C, $t_{g2} \approx 210$ °C).

The destruction of the chitin proceeds in two stages (t_{destr1}290 °C and $t_{destr2} \approx 325$ °C) with the absorption of energy in the form of heat (***Table 1, Figure 1***).

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