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THERMOANALYTICAL STUDIES ON LOBSTER SHELL

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Thermoanalytical investigations have been performed on lobster shell, its main components (chitin and protein) and the influence of the isolation procedure. The different peaks appearing during the thermal decomposition of lobster shell were identified, except for an endothermic peak at 220°. A hypothesis is suggested for the nature of this peak.

One of the principal lines of the Cuban fishery industry is the lobster. More than the 20% of the crustacea consists of the shell, from which chitin, protein and salts can be obtained. These substances are very useful in the pharmaceutical, textile and food industries. Lobster shell has been studied previously by biological and chemical methods [1, 2] and its composition is known (Table 1).

The aim of this study was to obtain additional information on lobster shell and its main components by means of thermoanalytical methods. Further, the influence of the processing on the components within the shell has also been characterized.

Experimental

Materials

Shell was studied from the lobster Panulirus argus, captured in July 1979 in the Batabano Gulf, in the south of Cuba. Chitin was obtained by the method of Henriques [3], and the soluble protein was extracted according to Oviedo [4].

Methods

Thermal analysis was performed with a derivatograph and Q-derivatograph. The sample weight varied in the range 50–270 mg. The heating rate was 3–5 deg/min and the atmosphere was air or nitrogen.

IR measurements were performed with a UR-10 instrument. Mass spectroscopic measurements were carried out with a Jeol-01SG-2 instrument.

Table 1 The main composition of lobster shell

Components	Percentage
humidity	11
protein	15
chitin	16
ashes	52

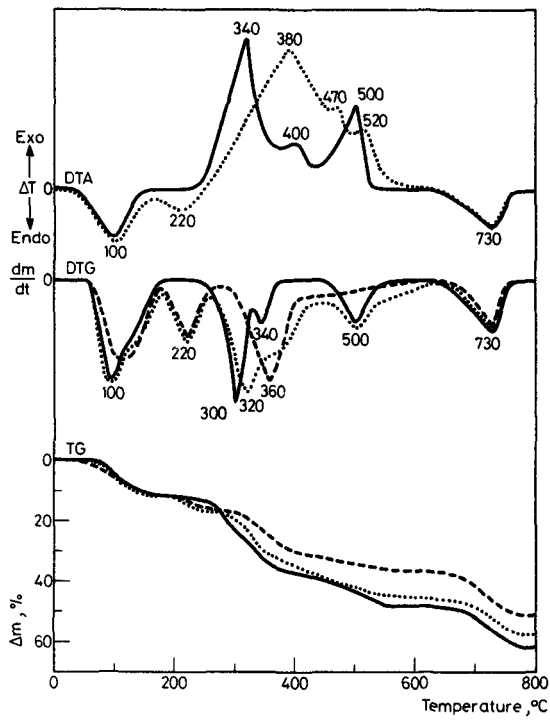

Fig. 1 Thermoanalytical curves of lobster shells: a ——— Fresh lobster shell in air; b . . . . . Stored lobster shell in air; c — — — — Stored lobster shell in N_2

Results and discussion

The thermal curves of lobster shell are presented in Fig. 1. The first endothermic peak, at about 100°, with a weight loss of 11%, is due to the elimination of water. Under quasi-isobaric quasi-isothermal conditions in an inert atmosphere, this process was resolved into two steps: below 40° the absorbed water was released, resulting in

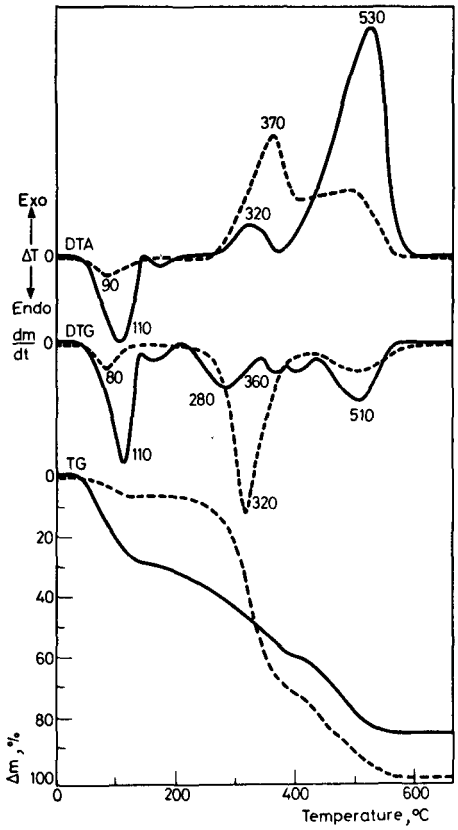

Fig. 2 Thermoanalytical curves of protein and chitin obtained from lobster shell: ———— protein; — — — — chitin

a 6.2% weight loss, while above 40° the departure of structural water took place, resulting in a 4.5% weight loss. Subsequent decomposition of the sample occurred between 180° and 760°. In the DTG curve of fresh lobster shell (Fig. 1a) peaks could be observed at 300°, 340°, 500° and 730°. The DTA curve revealed that the first three of these decomposition processes, probably relating to the degradation of proteins and pigments [5], were exothermic, while the 730° peak, probably due to the decomposition of inorganic compounds, was endothermic in nature. It could be demonstrated with the Q-derivatograph that the inorganic content consists of Ca and Mg carbonates and phosphates. In the decomposition curves of lobster shell stored for several months an additional endothermic peak can be observed at 220°.

Figure 2 presents the decomposition of the isolated components (chitin and proteins). In both samples the water content is lost in the range 20–150°, with the DTG peak temperature at 80 and 120° in chitin and protein, respectively. The main decomposition process of chitin occurs at 320°; this might correspond to the similar process

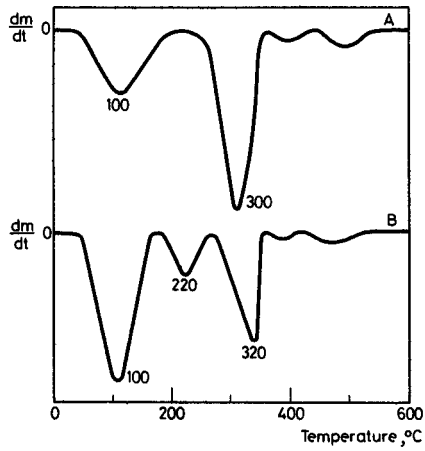

Fig. 3 DTG curves of the lobster shell stored within different conditions. A: no light, no humidity, 25°C; B: light, 80% rel. humidity, ambient temperature approx. 40–50°C

observed for the original lobster shell. The decomposition of protein takes place in two main steps: the first, at 280°, is probably due to the cleavage of peptide linkages and the formation of secondary products, and at 510° the decomposition of these secondary products is completed [6].

When the decomposition curves in Figs 1 and 2 are compared, all the DTG peaks in the decomposition curves of the fresh lobster shell can be identified on the basis of the decomposition curves of the isolated components. An additional peak was found at 220° in the DTG curve of the stored shell, and it might be suggested that this is due to some interaction between the chitin and the protein during the storage at high humidity. In order to shed light on this phenomenon, the influence of humidity, light and elevated temperature during the storage of the lobster shell on the thermal behaviour was studied. The shells were stored for 4 months in PE bottles, in the presence or absence of light, at ambient temperature and humidity, and also above P_2O_5. The results obtained on thermal analysis are presented in Fig. 3. It is to be seen that storage in high at ambient humidity and temperature results in the appearance of the DTG peak at 220°. From this observation it was assumed that the DTG peak at 220° relates to a reaction between the lobster shell components. For further classification, model experiments were performed with mixtures of glucosamine (the monomer of chitin) and protein. The two components were mixed in aqueous solution in a ratio of 7:3, which corresponds to the ratio of the components within lobster shell. As can be seen in Fig. 4a, in the 220° region no decomposition peak appears in the protein curve. For glucosamine, two peaks at 200 and 225° indicate a thermal process within the molecule (Fig. 4b). This decomposition was more marked when glucosamine was mixed with protein (Fig. 4c). To identify the nature of this reaction, IR spectroscopy was carried out (Fig. 5). For the 7:3 mixture a shoulder

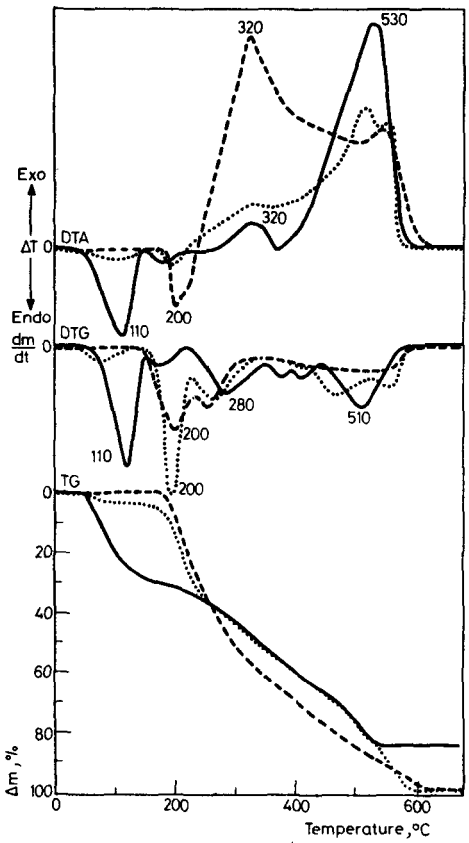

Fig. 4 Thermoanalytical curves of a ——— lobster shell protein; b – – – – glucosamine; c . . . . . mixture of glucosamine:protein = 7:3

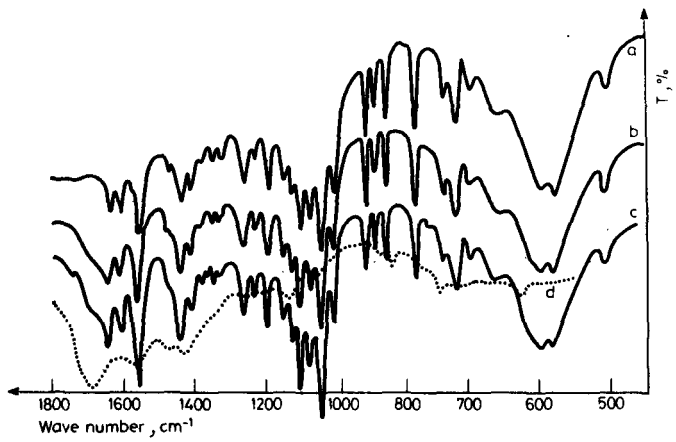

Fig. 5 IR spectra of the components of the lobster shell: a glucosamine; b glucosamine + protein; c glucoamine + protein treated up to 150°C; d protein

appeared at 1680 cm^{-1}, probably due to the formation of a new N=C bond as a consequence of a reaction between the NH_2– groups of glucosamine and the –COOH groups of the protein:

$$-NH_2 + O=C\diagup\diagdown \longrightarrow -N=C\diagup\diagdown + H_2O$$

This condensation between glucosamine and protein could be intensified by heating to 150°. Similar reactions might easily take place between the polysaccharide and the protein moiety of lobster shell as well during storage.

The results discussed above permit some practical conclusions concerning the processing of lobster shell (e.g. attaining optimum extractibility of soluble protein, avoiding browning of chitin, etc.).

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Zusammenfassung – Seekrebsschild, dessen Hauptbestandteile (Chitin and Protein) und der Einfluss des Isolationsverfahrens wurden thermoanalytisch untersucht. Die während der thermischen Zersetzung des Seekrebsschildes erscheinenden verschiedenen Peaks wurden mit Ausnahme eines endothermischen Peaks bei 220° identifiziert. Für die Art diesen Peaks wurde eine Hypothese empfohlen.

Резюме – Термоаналитические исследования были применены для исследования панцыря рака и его главных компонент – хитина и протеина, а также влияние метода их выделения из ракообразных. Идентифицированы различные пики, появляющиеся во время термического разложения панцыря рака, за исключением эндотермического пика при 200°. Выдвинута гипотеза и природе этого пика.