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Effects of thermal treatments on the structure of two black coral species chitinous exoskeleton

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Abstract Black corals (Antipatharians) are colonial cnidarians whose branched tree-like skeleton is constituted of chitin fibrils inside a lipoproteic matrix. The arrangement of the constituents of these materials provides a structure with outstanding physical properties. In this study, the structural properties of black coral skeletons of *Antipathes caribbeana* and *Antipathes pennacea* species are explored by means of thermal treatments in the range from room temperature up to 400 °C and the subsequent analysis using X-ray diffraction (XRD), infrared spectroscopy (FTIR), and thermal analysis (DSC/TGA). The effects of thermal treatment from room temperature up to around 210 °C induce the enhancement of the bands in the FTIR spectra and X-ray diffractograms, above that temperature, the FTIR and X-ray peaks become strongly attenuated. These effects are specially observed in the infrared bands associated to chitin at 3298 cm^{-1} and to the secondary amide stretching around 1663 cm^{-1}, in particular, allowing the identification of the α-chitin in the black coral. XRD shows that the crystallinity index of the black coral chitin at room temperature is 24% and grows when the temperature increases, reaching a maximum value of 37% at 210 °C and decreases for higher temperatures. In addition, DSC and TGA measurements allowed identifying the most important transformation stages during the thermal treatments, namely, evaporation of water and the beginning and progress of degradation, depolymerization, and denaturation processes and finally, the degradation of the main functional groups of coral skeleton and coral chitin, in which the polysaccharide structure of chitin is depolymerized and the protein matrix is denatured.

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Introduction

Antipatharia order, thorny or black corals, possesses by now about 230 valid species living in all oceans, in depths ranging from shallow water to thousands of meters [1]. Antipatharians are colonial cnidarians that frequently show arborescent appearance characterized by a spiny and branched skeletal axis made of material mainly composed by chitin [2]. *Antipathes caribbeana* and *Antipathes pennacea* are black coral species commonly are found at deep reefs of Cozumel Island (western Caribbean); the skeletons of these species are composed primarily of chitin fibrils incorporated in a lipoproteic matrix.

Chitinous structures are known to be present in at least 19 animal phyla [3]. Chitin can appear as ordered crystalline microfibrils forming structural components in the exoskeleton of arthropods as well as in the cell walls of fungi and yeast [4]. Chitin is a linear polysaccharide ((1 → 4)-linked *N*-acetyl β-D-glucosamine). It is one of the most abundant biopolymers. Its structure is similar to

cellulose, but it is different in that it has an acetamide group instead of a hydroxyl group at the C-2 position within the glucose unit [5].

Biopolymers, in particular chitin, are susceptible of structural changes due to temperature treatments. The thermal properties of chitin are determined by several factors: source and sample type (e.g., animal, fungi, cuticle, skeleton, shells, antennae, mandible, and extremities), water content [6], degree of deacetylation [7], heating rate and atmosphere (argon, nitrogen, oxygen, water, etc.), [8, 9] and finally the crystalline structure (α, β, and γ) [5]. The most commonly found crystalline phase associated with these structures corresponds to α chitin [10].

The conformational transformation studies of black coral represent a biomimetic model study of great importance academically to understand the crystalline structure, molecular fibrillar arrangement, and thermal behavior of chitin. In particular, the knowledge of the degradation process of chitin extracted would allow improving the understanding of its structural roll in the antipatharian skeleton.

In materials science, thermal treatments have proven to be a useful tool for understanding the conformation, structure, and transformation of a wide variety of materials. In this study, the effect of thermal treatments on the skeletons of *A. caribbeana* and *A. pennacea* is examined. The temperature range was selected considering that the most important thermal changes of chitin occur from ambient temperature to 400 °C [5]. The evolution of the material is monitored using Fourier Transform Infrared (FTIR) spectroscopy and X-ray diffraction (XRD). In addition, our studies have been complemented by differential scanning calorimetry (DSC) measurements. In order to quantify the involved changes in the loss of material, thermograms were obtained using thermogravimetry (TGA).

Experimental

Materials

Black coral colonies of the species, *A. pennacea* and *A. caribbeana*, were provided by the Federal Office for Environmental Protection Office of Quintana Roo, Mexico (Western Caribbean). The colonies were collected from the deep reefs of Cozumel Island.

Preparation of black coral chitin

Cuts of colony fragments between 4 and 8 cm in length were obtained near the base of the main stem. Samples were prepared grinding the black coral samples in a ceramic mortar until a very fine powder was obtained. First of all, the powder was processed by treatment in HCl and NaOH. The obtained material was demineralized with 0.25 M HCl at room temperature (25 °C) during 3 h, with a raw material ratio of 5 g/200 mL. Then, the material was washed with distilled water, filtered with negative pressure, and dried. Deproteinization was carried out with aqueous solution of 1 M NaOH at 65 °C for 24 h and then washed with distilled water, filtered with negative pressure, and dried in an oven under static vacuum at 70 °C. This process was repeated for three different colonies of each species. From black coral skeleton was obtained of chitin powder 14.9% in *A. pennacea* and 11.8% in *A. caribbeana*.

Samples were thermally treated for 1 h in an electric furnace at several temperatures: 110, 210, 270, and 310 °C, afterward, they were cooled at room temperature. FTIR and XRD analyses were made after each thermal treatment.

Infrared analysis (FTIR)

IR Spectra in the transmittance mode were recorded on a Thermo Nicolet Nexus 670 FTIR spectrometer equipped with a DTGS KBr detector in the middle infrared (4000–400 cm^{-1}). Samples of powdered black coral skeleton and chitin samples (5 mg) were mixed thoroughly inside an agate mortar with potassium bromide (95 mg) until homogenization. This mixture was inserted into the sample compartment of the spectrometer and continuously purged with dry air. The number of scans for each spectrum was 64, and the spectral resolution was 4 cm^{-1}.

XRD

XRD patterns were obtained with a 2100-Rigaku diffractometer using a monochromatic CuK_{α} radiation ($\lambda = 1.518$ Å), operating at 40 kV and 35 mA. The specimens were registered in a zero background sample holder to avoid external background interferences. The diffractograms were registered in the range of $4° < 2\theta < 60°$ in a step scan mode of 0.02° (2θ) with a counting time of 12 s per step.

DSC

Measurements of DSC were carried out using a DSC 822 Mettler Toledo equipment. Accurately weighed material was placed inside an aluminum cup of 40 μL capacity and hermetically sealed. A heating rate of 10 °C/min was used while the sample is inside an argon atmosphere with a flux of 50 cc/min.

Thermogravimetric analysis (TGA)

A Mettler Toledo TGA/SDTG 851 apparatus was used to assess the weight loss with heat treatment. Accurately weighed material was placed inside an aluminum cup and

hermetically sealed. A heating rate of 10 °C/min was used inside an argon atmosphere (50 cc/min) from 20 to 500 °C.

Results and discussion

FTIR spectrometry analysis

FTIR spectra of *A. caribbeana* and *A. pennacea* corals samples show the presence of chitin. Figure 1 shows the FTIR spectra of the chitin extracted from both coral samples and the spectrum of a standard α-chitin (from crab shells, Sigma-Aldrich Lab.). The main bands of the black coral chitin including the corresponding functional groups and vibration modes are summarized in Table 1. At high wavenumbers two bands at 3448 and 3290 cm^{-1} can be observed. They are associated with structural aromatic ring of the chitin molecule; the first is related to OH stretching mode of hydroxyl groups, and the second to N–H stretching vibration mode of the amide groups. In addition, FTIR spectra exhibit several small bands at 3093, 2933, and 2873 cm^{-1}; the first one corresponds to amide II and the other ones to aliphatic compounds, CH_2 and CH_3 with asymmetric and symmetric stretching vibration modes.

In the middle wavelength range, from 1660 cm^{-1} up to 1000 cm^{-1}, the bands are associated to the contribution of amides I, II and III, to saccharide ring, to phosphodiesters groups and proteinaceous components. Specifically, at 1660, 1639, and 1550 cm^{-1}, the characteristic bands of the functional groups of α-chitin were detected. It is important to mention that some bands registered in the black coral skeleton could be associated with some signals of β-chitin

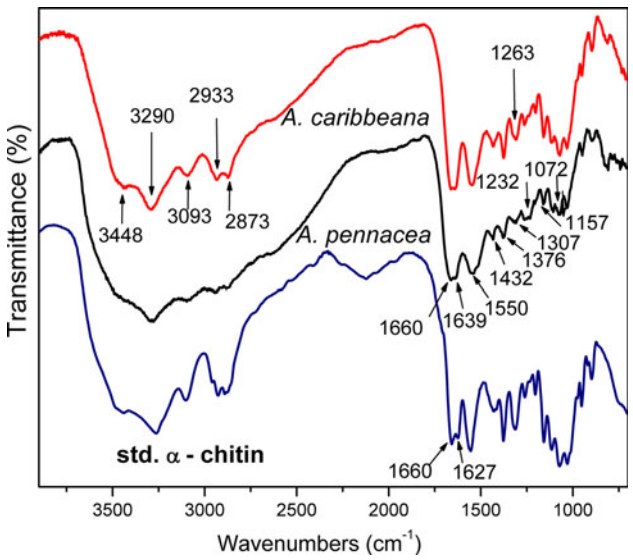

Fig. 1 FTIR of black coral chitin of two species and standard α-chitin from crab shells

structure. However, FTIR spectra show stronger coincidence with α-chitin structure. In Table 1, the wavenumber for each type of chitin vibration mode (α or β) has the appropriate label. The band at 1307 cm^{-1} can be related to proteins or CH_2, with wagging vibration mode. Near 1200 cm^{-1}, particularly at 1232 and 1072 cm^{-1}, the characteristic bands corresponding to phosphodiester groups with asymmetric stretching of PO_2^- are observed. In addition, the band at 1203 cm^{-1} is associated to oligo and polysaccharide with C–O–C, C–O–P, P–O–P symmetric stretching vibration mode. In the low wavenumbers range, deformation and stretching vibration modes at 948 and 896 cm^{-1}, corresponding to signals of CH_3 and CH associated to the aromatic ring of chitin, can be observed.

When the thermal treatment is applied, FTIR measurements showed that in coral and chitin for both species, *A. caribbeana* and *A. pennacea* coral, infrared bands in the whole range of wavenumbers are enhanced slightly in sharpness and size up to 210 °C, but at higher temperatures, most of the bands begin to decrease, and they are nearly suppressed at 310 °C. In particular, the band at 830 cm^{-1} remains constant independently of the thermal treatment and could be related to the presence of inorganic groups, such as nitrates, carbonates, sulfates, or silicates [14] that are commonly found in sea water. It is important to observe that this peak only appears in coral samples (Fig. 2a, b).

In the case of chitin (Fig. 2c, d), the behavior is different, the bands in the range from 4000 to 2500 cm^{-1}, increase with heating, enhancing their intensity and sharpness up to 210 °C, above 270 °C those bands are strongly attenuated. Particularly, FTIR spectra of chitin showed a peak at 3298 cm^{-1} in *A. pennacea* and 3291 cm^{-1} in *A. caribbeana* assigned to N–H stretching (secondary amide), but broader and moved to a lower wavenumbers. This behavior has been associated with an increase on the degree of deacetylation of chitin [15], and implies a decrease of the intermolecular forces within molecules of half-deacetylated chitin, with the free hydroxyl groups, amino groups, and the polymer chain end readily bonding with water. This effect is most noticeable for chitin of *A. pennacea.*

Interesting results can be observed in the range from 2000 to 1000 cm^{-1} for *A. pennacea* and *A. caribbeana* chitin, an enhancement of the peaks at 1663 cm^{-1} for *A. pennacea* and 1670 cm^{-1} for *A. caribbeana* assigned to C=O stretching (secondary amide) when the temperature is under 270 °C, for higher temperatures, most of the bands decrease and shift, disappearing for the highest temperature. The band around 1650 cm^{-1} for *A. pennacea* and *A. caribbeana* coral shows an enhancement of its intensity and sharpness before 270 °C, showing a shoulder at 1627 cm^{-1} similar to the standard α-chitin. In this sense,

Table 1 FTIR of the main signals of black coral chitin

Functional group and vibration modes	Classification	Wavenumber (cm^{-1}) frequency
O–H hydroxyl stretching	Water	3448[a]
N–H secondary amine asym. stretch	Amide	3290[b]
N–H secondary amide asym. stretch	Amide II	3093[b]
CH_3 asym./sym. stretch and CH_2 asym. stretch	Aliphatic compounds	2933[b]
CH_3 sym. stretch and CH_2 asym. stretch	Aliphatic compounds	2929[a,b]
CH sym. stretch	Aliphatic compounds	2873[b]
CH_3 sym. stretch	Aliphatic compounds	2883[a]
C=O secondary amide stretch	Amide I	1660[a]
C=O secondary amide stretch	Amide I	1662[a]
C=O secondary amide stretch	Amide I	1639[a]
N–H bend, C–N stretch	Amide II	1550[a]
CH_2 ending and CH_3 deformation	–	1432[a]
CH bend, CH_3 sym. deformation	–	1376[a,b]
CH_2 wagging	Amida III, components of proteins	1307[a]
NH bending	–	1263[b]
P=O asym. stretch of PO_2^-	Phosphodiester	1232[a]
C–O–C, C–O–P, P–O–P sym. stretch	Oligo and polysaccharide	1203[a]
C–O–C asym. stretch in phase ring	Saccharide rings	1153[a]
C–O asym. stretch in phase ring	–	1112[a]
C–O, P = O, sym. stretch of PO_2^-	Phosphodiester	1072[a]
C–O sym. Stretch	–	1032[b]
CH_3 deformation	–	948[b]
CH ring stretching	Saccharide rings	896[a]

[a] Bands coincident with signals of α-chitin; [b]Bands coincident with signals of β-chitin [5, 11–15]

–No literature reported

the thermal treatment reveals the presence of α-chitin, but without using a purification process to extract it. A comparison with FTIR spectrum of chitin standard is presented in Fig. 3, in which both bands (1660 and 1627 cm^{-1}) can be clearly observed.

CO stretching bands 1159, 1072, and 1028 cm^{-1} become sharper for thermal treatments under 210 °C, and are wider or disappear for higher temperatures. These last changes have been associated to the reduction of the deacetylated fraction of chitin samples [16, 17].

Bands at 896 and 1153 cm^{-1} have been assigned to the saccharide structure, and their appearance occur when temperature grows, decaying for higher temperatures, following the rupture of the β-glycosidic linkages between the glucosamide and the *N*-acetylglucoamine [18, 19].

XRD

It is well known that chitin is a semicrystalline polysaccharide polymer, as can be seen in the XRD patterns of chitin of black coral skeleton of both species, in comparison to the standard commercial α-chitin (Fig. 4). The powder patterns exhibit the characteristic crystalline reflexions associated to chitin, with peaks at 9, 12, 19, and 26° (2θ), and the indexed *hkl* planes are presented in Table 2. Both species showed the main peak of chitin at 19° (2θ), which is related to the *hkl* (110) planes. However, the crystalline reflexions show higher intensity in *A. caribbeana*, than in *A. pennacea*. The unit cell parameters were determined considering the orthorhombic $P2_12_12_1$ symmetry of chitin [20, 21] and the obtained values confirmed that the chitin of black coral exhibited an α crystalline structure. The crystallographic parameters of chitin are summarized in Table 2.

X-ray patterns for the powdered coral untreated samples (US) (Fig. 5a, b) show an amorphous background structure in which several small peaks within the range of 17°–35° (2θ) can be observed. However, *A. caribbeana* has wider and stronger peaks with a maximum around 12° (2θ), indicating that this species presents ultrastructural arrangement of chitin fibers with a stronger package as compared with *A. pennacea* [22]. Afterward, the crystallinity increases up to 210 °C and at higher temperatures the bands become wide and small and for higher temperature only a very wide band around 22° (2θ) remains.

The crystal structure changes notably after removal of the acetyl groups from coral (conversion to chitin). The thermal behavior of chitin is similar for both species

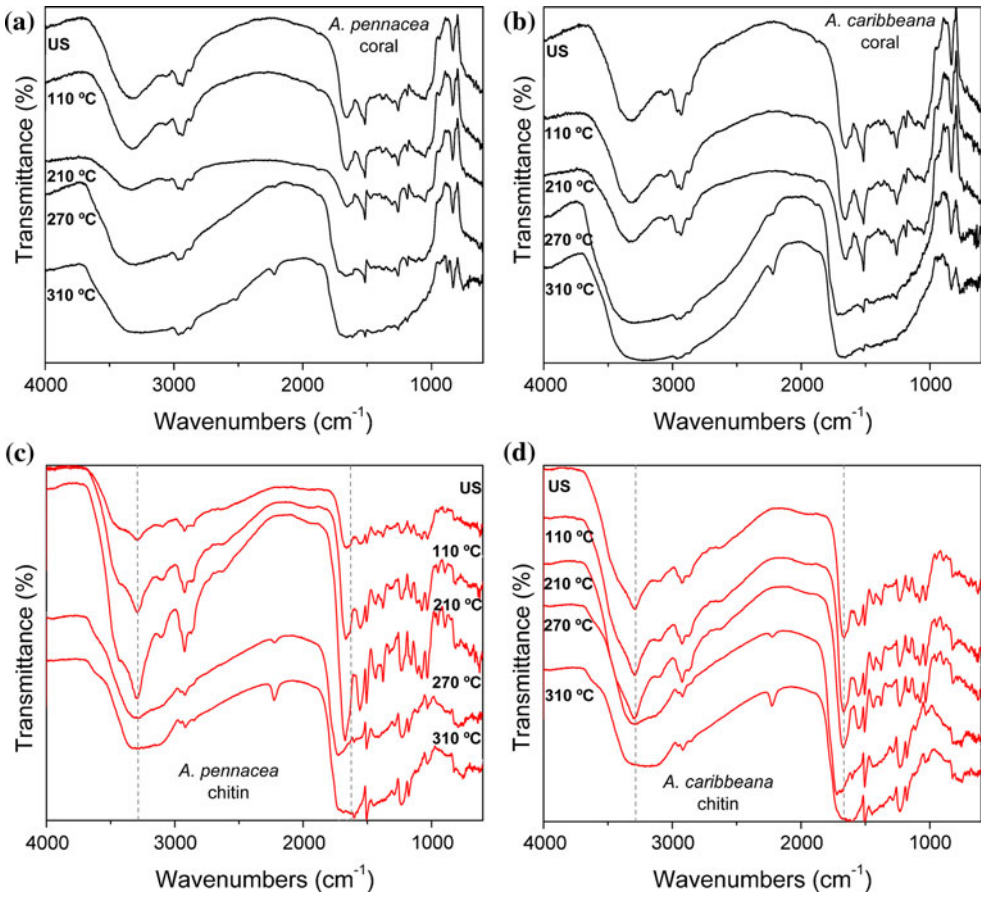

Fig. 2 FTIR spectra of black coral and extracted chitin with different thermal treatments (US-untreated sample, 110, 210, 270, and 310 °C). **a**, **b** Coral skeleton of *A. pennacea* and *A. caribbeana*; **c**, **d** Coral chitin of both species

(Fig. 5c, d). Predominantly, the intensity of peaks at 9° and 19° (2θ) increases up to 210 °C, indicating a more ordered structure, subsequently at higher temperature the polysaccharide crystalline structure is systematically destroyed.

In addition, the crystalline index of the chitin samples was analyzed using the peak at 19° (2θ). This choice was done based on the fact that this peak corresponds to the *hkl* (110) plane. In order to calculate the crystallinity index (CI), a method which has been previously used for cellulose is used. In this case, the CI is given by the expression [20, 23]:

$$\mathrm{CI}\% = [I_c/(I_c + I_a)] \times 100$$

where I_c represents the crystalline region in 19° (2θ) corresponding to the *hkl* (110) plane; and I_a the amorphous region, obtained from the XRDs patterns.

The results for the CI are shown in Table 3. It can be observed that CI for the untreated chitin is around 24% for both species and increases when the thermal treatment is applied obtaining a maximum value at 210 °C, being the highest CI for *A. caribbeana* (37%) than the value for *A. pennacea* (34%). This effect is due to the thermal treatment, as is usual in material science, where the thermal treatments in specific ranges of temperature are used to increase the crystallinity [21]. Afterward, CI decreases to 23% for *A. caribbeana* and 21% for *A. pennacea* indicating an increase in the structure disorder, which involves a clear tendency to generate an amorphous structure.

DSC

DSC curves of the black coral skeleton *A. caribbeana* and *A. pennacea* exhibit several endothermic peaks, being the stronger and wider ones around 118 and 298 °C. In addition, DSC thermograms of chitin in both species are very similar (Fig. 6), although in the case of *A. pennacea* better defined peaks were obtained. The differences in the DSC thermograms of black coral skeleton and its corresponding extracted chitin are due to the complex material of black coral since is made of chitin but also contains a mixture of other different substances as lipids, proteins, etc.

The first peak around 110 °C in coral and 118 °C in chitin are related to loss of water (dehydration process). Chitin is a polysaccharide, which usually has a strong water affinity, and in the solid state these macromolecules may have disordered structures which can be easily hydrated and dehydrated [7]. The higher temperature peak around 298 °C for coral and 306 °C for chitin is due to a thermal transition associated to the decomposition of the polymer structure [8]. The peak at 118 °C for chitin related to

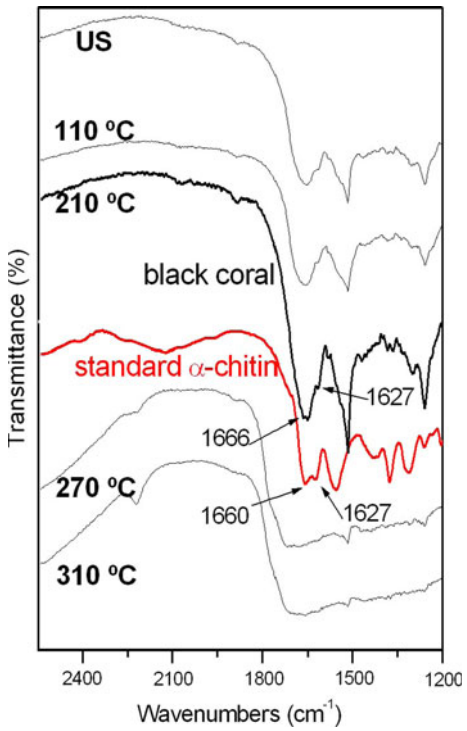

Fig. 3 A detail of FTIR spectrum from Fig. 2b. Spectra comparison of standard α-chitin and black coral, emphasizing the thermal treatment to 210 °C

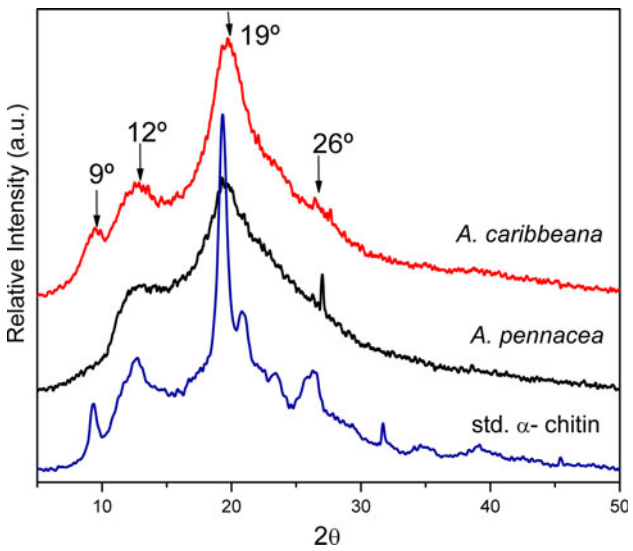

Fig. 4 X-ray diffractograms of black coral chitin of two species and a comparison with the standard α-chitin

dehydration is wide and high, implying that the change in enthalpy during this process is larger, even compared with the change of enthalpy occurring around 306 °C, associated with the chitin matrix degradation [7]. In the range from 200 up to 250 °C, minor endothermic peaks that can be attributed to the beginning of denaturation and degradation are observed [24].

TGA

TGA results for both species of black coral and extracted chitin show that the weight decreases with temperature. DTG curves show that the weight loss follows two well-defined stages (Fig. 7). The first one registered around 71 °C in *A. caribbeana* and 67 °C in *A. pennacea*, with a weight loss of 6.5 and 4.5%, respectively. The second stage was observed around 307 °C in *A. caribbeana* and 309 °C in *A. pennacea* with a weight loss of 13 and 9.3%, respectively. TGA and DTG curves behavior of chitin are similar to the corresponding black coral. The weight loss and the related temperatures for the different stages for both chitin species are similar, the first one has an average weight loss of 7% around 66 °C; however, for the second stage registered at the same temperature of 321 °C, different weight loss is observed for *A. caribbeana* is 32. 5% and for *A. pennacea* chitin is 20.7% (Fig. 7c, d).

From DTG curves, it is possible to recognize two peaks associated to the most important thermal transformations. In black coral skeleton as well as extracted chitin, the first transformation was observed between 66 and 71 °C, corresponding to the evaporation of water, which represents a weight loss of 5% for coral and 7% for chitin, this transformation is a common thermal transition in chitinous structures [7, 17, 25, 26]. Chitin is more easily hydrated than black coral skeleton; therefore, chitin is classified as a moderately hygroscopic material [27]. DTG shows several dehydration processes within a temperature range from 28 up to 125 °C. Initially, the superficial water present in the skeleton and chitin is easily lost at low temperature, around 50 °C, a small shoulder can be observed in Fig. 7c. Subsequently, evaporation of the secondary OH from the CH_2OH groups occurs, from 66 up to 71 °C. Finally, when the temperature rises above 100 °C the total dehydration is observed, since the structural water is eliminated from the OH directly linked to the saccharide ring, this can be clearly detected as a small shoulder around 110 °C (Fig. 7b). These dehydration processes can be related to DSC response that includes all thermal transformations since broad endothermic peaks at 110 °C for coral and 118 °C for chitin were observed.

The second stage peak shows a temperature range from 250 °C up to 350 °C for all the samples, and can be related to the beginning and progress of several processes such as degradation, depolymerization, and denaturation. In this thermal transformation, the aliphatic compounds (CH_2, CH_3 functional groups) are separated from the chitin structural ring, and after 323 °C, the amides groups I and II (C=O, N–H), the saccharide structure (C–O–C, C–O–P, and P–O–P), and the phosphodiesters groups (CO, P=O, and PO_2^-) were degraded. This peak with a lower negative enthalpy shows a large weight loss average of 11% for coral and 26% for chitin.

Table 2 Crystallographic parameters of black coral chitin in comparison to the standard commercial α-chitin

Species	2θ (°)	(*hkl*)	*d*-spacing (Å)	Unit cell parameters (Å)
A. caribbeana	9.4	(020)	9.51	$a = 4.66$
	12.5	(021)	7.08	$b = 19.01$
	19.6	(110)	4.53	$c = 10.60$
	26.3	(013)	3.38	
A. pennacea	12.7	(021)	7.03	$a = 4.72$
	19.2	(110)	4.58	$b = 19.01$
	26.9	(013)	3.30	$c = 10.42$
Standard α-chitin	9.28	(020)	9.53	$a = 4.74$
	12.66	(021)	6.99	$b = 19.06$
	19.3	(110)	4.59	$c = 10.29$

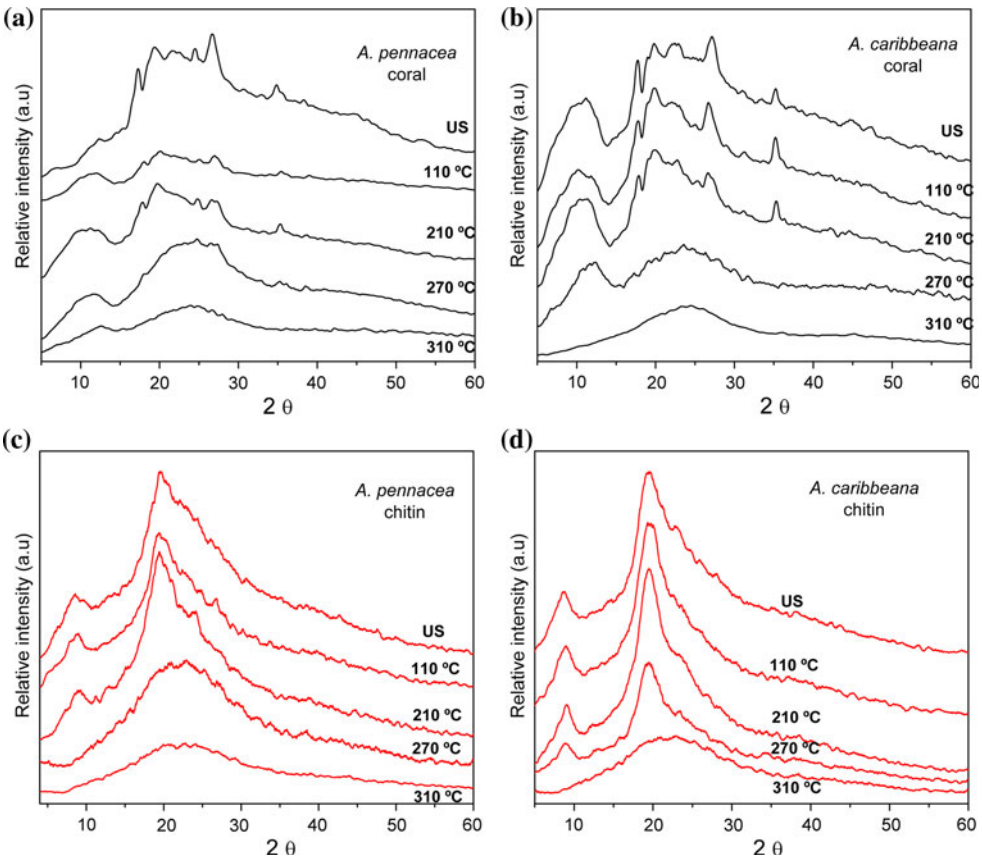

Fig. 5 X-ray difractograms of black coral and extracted chitin with different thermal treatments (US-untreated sample, 110, 210, 270, and 310 °C). **a**, **b** Coral skeleton of *A. pennacea* and *A. caribbeana*; **c**, **d** Coral chitin of both species

Table 3 Crystalline index of black coral chitin as a function of thermal treatment

Temperature (°C)	Crystalline index (%)	
	A. pennacea	*A. caribbeana*
US	24	25
110	25	29
210	34	37
270	24	25
310	21	23

The results of thermogravimetric analysis (DSC, TGA, and DTG) show that the skeletons of *A. caribbeana* and *A. pennacea* and their extracted chitin decompose within the temperature range of 300 °C up to 400 °C, near to the reported temperature in the literature for other chitinous structures [7, 17, 26, 28]. It is important to mention that the black coral chitin is degraded around 300 °C, in contrast the standard α-chitin from crab shells (Sigma-Aldrich Lab) which is degraded at 350 °C, in addition the reported value for γ-chitin from squid is that the degradation occurs at 300 °C [7] that is similar to the values obtained for coral chitin. However, the thermal

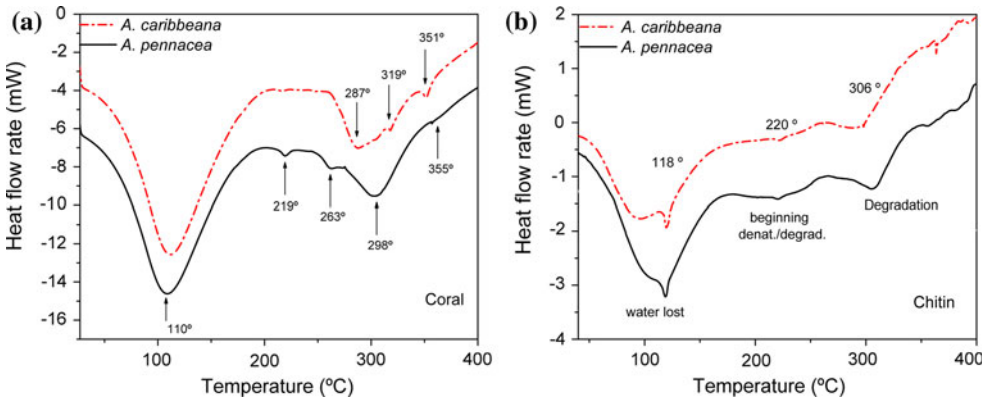

Fig. 6 DSC thermograms of two black coral species. **a** Coral skeleton; **b** Extracted chitin from coral

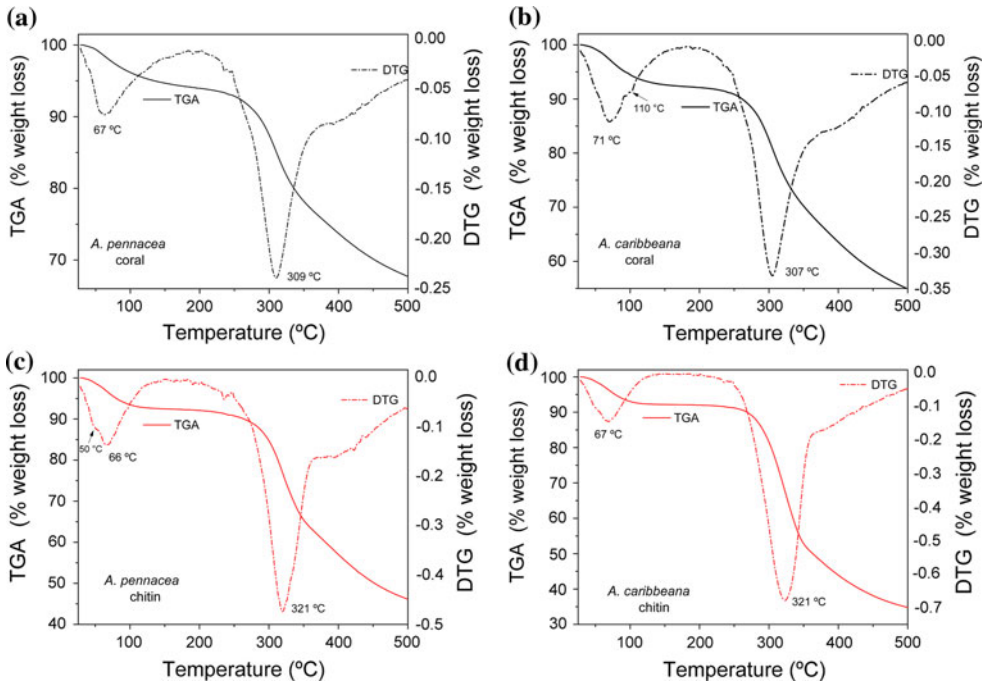

Fig. 7 TGA thermograms and DTG curves. **a**, **b** Coral skeleton of *A. pennacea* and *A. caribbeana*; **c**, **d** Coral chitin of both species

properties of biopolymers as chitin, specifically the degradation temperature, depend strongly on diverse factors, such as the source and sample type, as well as purity and degree of deacetylation among others.

Comparing DSC, TGA, and DTG results, it can be observed that the peaks associated to water are small for DTG and high for DSC indicating that the loss of a small quantity of water implies a moderately high change in enthalpy. In contrast, the peak associated to degradation of chitin is small in DSC and high in DTG, indicating that a high change of weight in this stage implies a lower change of enthalpy.

Conclusions

The effect of thermal treatment on black coral skeletons of *A. caribbeana* and *A. pennacea* species and its extracted chitin were analyzed using FTIR spectroscopy, XRD DSC, and TGA. The results indicate that the thermal treatment produces an enhancement of the infrared bands for thermal treatments below 210 °C, permitting to identify that the material has a α-structure. After this critical temperature, 210 °C, the bands are clearly attenuated. The behavior of the bands follows different processes in terms of deacetylation, disengaging of structures, and degradation. In addition, when the samples are thermally treated below 210 °C, the intensity of the peaks on the XRD pattern increases. This implies a change of crystallinity above 40% for the extracted chitin compared with the untreated samples for both species, and afterward the crystallinity is lost at higher temperatures.

These analyses were complemented with DSC and DTG studies allowing us to correlate and to shed light on the complex process occurring in the black coral and its corresponding chitin during heating. The obtained results

could be useful in the development of biomimetic chitin-based materials.

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