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DSC measurements on sharks

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Abstract

Sharks are commonly termed fish, even though they are only distantly related to the classical (bony) fish. What differentiates a shark from a bony fish? Sharks have a spinal column and are thus vertebrates. However, their skeleton is not made of bones, but of cartilage, and together with their nearest relatives the rays and the chimeras they form the class of cartilaginous fish.

Since the late 1980s trade in shark fin was considered to be one of the most valuable fishery products in the world. Another valuable shark product is cartilage. Shark meat has been used as food in coastal regions for over 5000 years. Small sharks are preferred for meat in many markets. In Germany, the belly flaps of spiny dogfish (*Squalus acanthias*) are smoked as "Schillerlocken", an expensive gourmet item. The question came up to us recently if we were able to detect whether shark muscle were heat-treated as in the case of smoking or not. Different tariffs for heated and untreated fishery products make it important for processors to label their products correctly. According to customs departments this necessitates investigations into whether the declaration of goods is true or not.

Looking at the relevant literature, papers dealing with thermal stability of shark muscle were very scarce. Therefore, we decided to perform DSC measurements on a variety of shark using a SETARAM MicroDSC VII and to compare the DSC patterns obtained. Beside thermal stability the colour of different shark meats were also measured instrumentally. To answer the question of whether DSC measurement can differentiate previously heat treated sharks from those lacking this treatment, the cutlets from smooth-hound (*Mustelus* spp.) underwent thermal treatment in the range from 40 to 70 °C. DSC patterns of the shark muscle and the skin were used to observe the influence of heat treatment.

Keywords: Shark; Differential scanning calorimetry; DSC; Heating of muscle; Skin

1. Introduction

Sharks are commonly termed fish, even though they are only distantly related to the classical (bony) fish. Over a period of more than 400 million years sharks have adapted themselves perfectly to life in the ocean and inhabit practically all ocean realms. What differentiates a shark from a bony fish? Sharks have a spinal column and are thus vertebrates. However, their skeleton is not made of bones, but of cartilage, and together with their nearest relatives the rays and the chimeras they form the class of cartilaginous fish [1]. Sharks and bony fish differ so much that it has been said "a human being and a frog are much closer to each other than a herring and a shark" [2]. Urea and trimethylamine in the blood and tissues of sharks help to maintain their osmotic balance. Urea must be removed by immediate bleeding, dressing and icing the shark after it has been caught to prevent urea from contaminating the meat. Urea is converted by bacteria to ammonia and lodges in the tissues. Improper handling causes a strong ammonia odour and taste. Due to urea and ammonia the shelf life of fresh products is limited to a few days. While 8–10 days [3] and 11–12 days [4] are reported as a maximum shelf life, only 6 days has been recommended recently [5]. However, it was found that gel forming ability of the shark meat showed marginal decrease during 12 days of ice storage and therefore shark meat can be used up to 12 days for gelled type of products like surimi [6]. An appropriate gelation-dependent process to prepare a convenient food product from shark meat was developed recently [7].

The life history of sharks is characterised by slow growth rates, low fecundity potential, relative late sexual maturation, long life spans. Therefore, they are classified by ecologists as strong K strategists [8]. On shark catch, no correctly reported data are available. According to the latest report, catches of the "sharks, rays, chimaeras" group have been stable since 1996 at about 0.8 million tonnes [9].

Sharks are a valuable resource and raw materials derived from sharks are found in many products. They are exploited

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for (a) meat (fresh, frozen, salted, smoked), (b) fins (one of the most expensive fishery products—famous shark fin soup in Chinese cuisine), (c) liver oil (cosmetics and pharmaceutics), (d) skin (leather and sandpaper), (e) teeth (jewellery), (f) cartilage that should be beneficial in the treatment of a great variety of diseases such as arthritis, psoriasis colitis, acne, enteritis, phlebitis, rheumatism, peptic ulcers haemorrhoids, herpes simplex, melanoma and above all cancer. Shark resistance to cancer has created a new market in alternative medicine, even though its benefits are unproved. FDA classifies shark cartilage as a dietary food supplement. A detailed overview on the utilisation of shark is given in [10]. Shark fins are one of the most expensive fish products in the world. They are used to prepare shark fin soup which is usually prepared by adding other ingredients for taste, such as chicken, crab or abalone. Shark fins have a traditional and virtually exclusive market among Chinese ethnic groups living in different parts of the world, but little elsewhere. The use of shark fins as food has been known in China for centuries. At present they are served at dinner parties to express the host's respect for his guests (e.g. weddings, parties for Chinese New Year). Taking into account the importance of shark fins in international trade a Codex Alimentarius Standard [11] has been created which characterise as defects: (i) sample unit exceeding 18% moisture and (ii) textural breakdown characterised by softness.

Shark meat has been used as food in coastal regions for over 5000 years. Small sharks are preferred for meat in many markets. Shark fillets may be salted and diced or smoked. In some countries it was necessary to camouflage the name shark under a number of euphemisms to overcome consumer resistance [8]. For example, in Germany, spiny dogfish backs (whole skinless, headed and gutted, bellies removed) are sold as "Seeaal" and hot smoked belly flaps (skinned and trimmed) as "Schillerlocken", an expensive gourmet item. Uncertainties in the evaluation by customs of whether shark muscle has been heat-treated exist. This is particularly problematic in the case of hot versus cold smoking. This uncertainty by customs has recently led to investigations by our department to establish if goods were declared truly. Different tariffs for heated and untreated fishery products make it necessary for processors to label their products correctly. As revealed by a review of the relevant literature, work on thermal behaviour of sharks is sparse. Only a group working in Taiwan has published any papers on DSC measurement made on sharks, and this was about 10 years ago [12–16]. Other papers deal with the thermal behaviour of collagen and gelatine prepared from shark skin. Here the authors compare shark skin thermal stability with that of pig skin [17–20].

To see whether there are differences in thermal behaviour between bony fish and sharks DSC measurements were performed using muscle and skin of shark. Furthermore, the influence of heating the shark has been investigated. The heating conditions employed have been designed to mimic those occurring during smoking. Therefore, the DSC curves obtained from unheated shark muscle and skin were compared to those from previously heated fish.

2. Experimental

2.1. Shark

Different sharks (catsharks, *Scyliorhinus* spp., smooth-hounds, *Mustelus* spp., liveroil sharks, *Galeorhinus* spp.) were caught by trawl net in the Lyme Bay, an area of the English Channel, in April 2005 during 274th research cruise of FRV "Walther Herwig III". Sharks were headed and gutted, deep frozen and investigated after around 3 months of frozen storage at −24 °C. Deep frozen and hot smoked samples of spiny dogfish (*Squalus acanthias*) were obtained from Hamburg fish market. The fish used for heating experiments was the smooth-hound. Four different specimens were used for this trial. The sharks were thawed overnight in a refrigerator at 4 °C and cut transversally to the back bone into cutlets, approximately 2.5 cm thick. One to two cutlets were packed in cooking bags and heated in a water bath (Haake 6P, Karlsruhe, Germany) at given temperatures in the ranges from 40 to 50 °C as well as 65 to 75 °C in 5 K intervals until core temperature was equal that of the water bath. Temperature was recorded during heating the samples using a temperature controller MD 3150 with automatic measured data storage unit 800 (Beckmann + Egle Industrieelektronik, Kernen, Germany). Cutlets were left for 15 min at final temperature and subsequently cooled down using ice-cold water prior to air-blast freezing at −24 °C. All frozen samples were stored for 2 months at same temperature until investigation.

2.2. Methods

2.2.1. Differential scanning calorimetric measurements

In the heat flux DSC (a Tian-Calvet type microcalorimeter), thermal effects are measured by two fluxmeters (one on the measurement side and one on the reference side), each of which measures the thermal power exchanged at each moment between the vessel and the calorimetric unit. The Tian-Calvet fluxmetric transducer envelopes the sample, making it possible to measure almost all the exchanges between the vessel and the unit. The differential power required to heat the sample compared to the reference at the same scan rate is thus recorded. This capability gives this device a clear metrological advantage in terms of both the quantity of measurements and their sensitivity (capacity to measure very weak effects) [21]. The equipment employing the aforementioned system was a MicroDSC VII (SETARAM, Caluire, France). Measurements were performed in duplicate as reported recently [21]. Results are displayed as average curves in the figures. The average curves are used to record the onset and transition temperatures (T_{on} and T_{max}) and to calculate the transition enthalpy (ΔH) expressed as $J\,g^{-1}$ sample material from the peak area using the SETARAM software SETSOFT 2000, version 1.6, rev. 4. Samples of ordinary muscle as well as of skin (300–500 mg) were weighed accurately (±0.1 mg) and heated from 25 to 95 °C with a scanning rate of $0.3\,K\,min^{-1}$.

2.2.2. Instrumental measurements for colour

Colour measurement were taken on cutlets using a spectral colorimeter Spectro Pen® (Dr. Lange, Düsseldorf, Germany)

Table 1
Proximate composition of shark meat

Species	Crude protein	Crude fat	Dry matter	Ash	pH
Catsharks	20.52	0.61	22.31	0.43	6.10
Smooth-hounds	18.39	0.68	20.37	0.57	6.42
Liveroil sharks	20.38	0.82	22.33	0.65	6.26

working in the CIELAB system. In this system, L^* denotes lightness on a 0–100 scale from black to white; a^*, (+) red or (−) green; b^*, (+) yellow or (−) blue. ΔE, the colour difference, denotes the square root of $(\Delta L^2 + \Delta a^2 + \Delta b^2)$. Performance of measurements has been described previously [22].

2.2.3. Proximate composition

The proximate composition of the sharks was determined by using the respective standardised German methods for pH, crude fat, ash, crude protein and dry matter [23].

3. Results and discussion

3.1. Comparison of sharks

According to their chemical composition sharks can be seen as rich in protein and poor in fat (Table 1). Values of protein, fat and dry matter are almost comparable with those reported for other shark species [6,24]. High nitrogen content found in shark meat is particularly caused by the non-protein nitrogen content which accounted for about 25% of the total nitrogen [6]. The pH values were reportedly species-specific [6], but can also be dependent on season, catching method, pre-slaughter stress, etc.

Shark meat also differed in colour as shown in Figs. 1 and 2. Liveroil shark was the lightest and reddest, while catshark was most yellow. Results of instrumental measurements taken on shark meat were not found in the literature so far. Colour difference ΔE^* between liveroil shark and smooth-hound was highest with 9.19 followed by ΔE^* between liveroil shark and catshark with 6.95 whereas ΔE^* between catshark and smooth-hound was small with 3.04.

The DSC patterns taken on the skin of the different sharks are shown in Fig. 3 and are characterised by one pronounced endothermic peak in the temperature region between 40 and 55 °C. It appears that thermal stability of catshark skin is lowest, whereas that of liveroil shark and smooth-hound are higher and comparable. The enthalpy of denaturation (ΔH) is generally high. Table 2 shows values for both onset

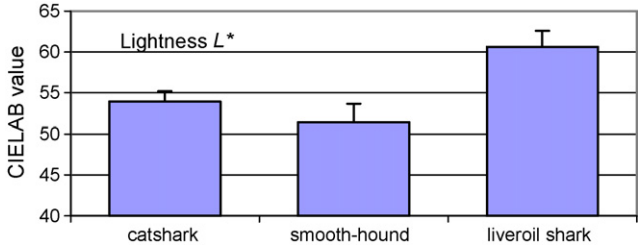

Fig. 1. Lightness of shark meat ($n = 20$).

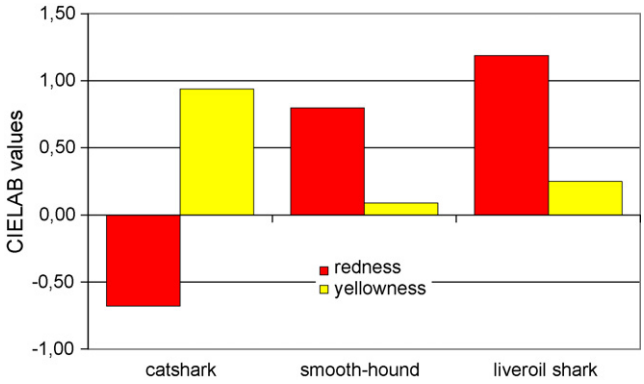

Fig. 2. Redness and yellowness of shark meat ($n = 20$).

and maximum temperature as well as for the denaturation enthalpy.

Among the aquatic animal collagen shark collagen is seen potentially important, and therefore their physicochemical properties were investigated and compared with those of pig type I collagen [17,19]. DSC curves of gels obtained from the different collagens showed a single peak that differed in their thermal stability depending on the origin of the collagen. DSC curve from shark collagen produced from blue shark skin indicated only one endothermic peak. The onset and peak top denaturation temperatures were estimated to be about 39 and 41 °C, respectively, with a range of about 3 °C. Results were comparable with those presented here, particularly with the catshark results. The DSC curve of pig collagen gel indicated a somewhat broader thermal transition occurring in a higher temperature region (about 58 °C) when compared with that of shark collagen [17]. The sharp and narrow peak for shark collagen gel suggests that a single highly co-operative endothermic reaction occurred. The

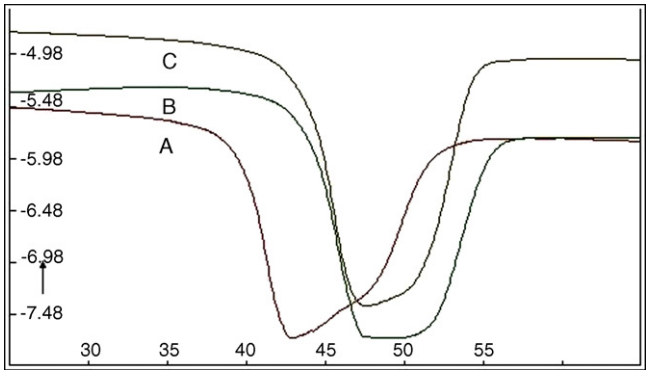

Fig. 3. DSC curves taken on skin of sharks (A) catshark, (B) smooth-hound and (C) liveroil shark; x-axis, furnace temperature (°C); y-axis, exothermic heat flow (mW).

Table 2
Denaturation temperatures (T_{onset}, T_{max}, °C) and denaturation enthalpy (ΔH, J g^{-1} wet weight) measured on shark skins

Species	T_{onset}	T_{max}	ΔH
Catsharks	39.8	42.9	9.2
Smooth-hounds	44.1	47.4	10.9
Liveroil sharks	43.8	47.5	12.1

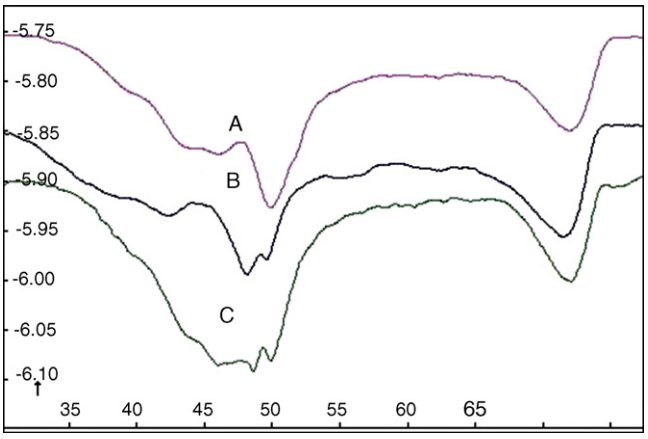

Fig. 4. DSC curves taken on muscle of sharks (A) smooth-hound, (B) catshark and (C) liveroil; *x*-axis, furnace temperature (°C); *y*-axis, exothermic heat flow (mW).

collagen-specific triple helical structure of shark type I collagen is similar to that of land mammalian type I collagen [17]. DSC was used to study the thermal behaviour of acidic solutions from different collagen species. These results indicated that collagen prepared from bird feed had the highest value (T_{onset}, 59.6 °C) of thermal stability. On the contrary, the collagen type I solution prepared from skin of scalloped hammerhead (*Sphyrna lewini*) showed the lowest transition temperature (T_{onset}, 44.7 °C). This value is almost comparable with those presented in Table 2. It is concluded that the amino acid composition directly influenced the thermal stability of different collagen species, the aquatic animal collagen contained lower prolin and hydroxyproline values and displayed a lower thermal stability [20].

Gelatine is a denaturation product of collagen and has been widely utilized for foods, photographic uses, medical materials, and microorganism culture materials. The DSC curve of shark gelatine gel as well as that of pig gelatine gel showed a single endothermic peak. The lower melting temperature of shark gelatine gel (21.8 °C compared with 28.5 °C for pig gelatine gel) indicated that the structural stability of shark gelatine was weaker than that of pig gelatine [18].

DSC curves of shark muscle are shown in Fig. 4. Assuming that the first main peak comprises myosin the one at higher temperature must be connected with actin. While the actin peaks are comparable sharp and narrow peaks the ones of myosin appear to be composite peaks. Denaturation temperatures and enthalpies of shark muscle proteins are demonstrated in Table 3. Denaturation temperatures of actin are almost comparable in muscles of the different sharks, whereas small deviations are to be seen for the both other peaks. The DSC pattern of shark muscle appeared to be species-specific. However, pronounced differences in thermal stability of the species investigated could not be expected because the environmental temperature of their living space was comparable. On the other hand, compared with DSC pattern taken on ordinary fish muscle such as that from sardine [25] it becomes obvious that T_{max} of the myosin peak is approximately 5 °C higher in shark muscle. In the DSC curves taken on the meat of sharks a small peak is to be seen in front of the myosin peak. Its transition temperatures and enthalpies are also displayed in Table 2. With the aim to identify the protein fraction that caused this peak, fibres of the connective tissue were dissected form whole muscle by the use of a scalpel (Fig. 5). The DSC curve taken on the fibres is shown together with the curves taken on the whole meat of catshark (Fig. 5). From the comparison of both peaks it becomes obvious that connective tissue appears to be responsible for the first small peak in the DSC curve of whole shark muscle. Differences in connective tissue amount in the shark muscle may have some impact on appearance of the DSC curve. The content of collagen in fish varies considerably from species to species and is found in increasing proportion in the tail region. In the main edible portion, concentrations of 0.3–3.0% are common [26]. Also some contribution from sarcoplasmic proteins particularly in the range between the major peaks of myosin and actin can be expected.

The following changes in shark muscle during heating by DSC analysis are assumed [12]: (i) changes in conformation of myosin molecules including solubilisation and denaturation of myosin tails might occur at a low temperature (30–43 °C), corresponding to the low endothermic peaks, (ii) at higher temperatures (47–57 °C), the head portion of the myosin molecule might project from the filament would enable more interactions among head portions. In DSC analysis of small hammerhead shark (*Sphyrna lewini*) muscle during cold storage at 5 °C an exothermic peak within 25–45 °C and a low temperature endothermic peak (LTEP) around 35 °C were observed after 8 and 56 h postmortem, respectively [13]. The exothermic peak between 30 and 40 °C observed for the unfrozen muscle and the LTEP disappeared in DSC pattern of muscle stored for 150 days. The longer the fish chunks stored, the sooner the LTEP or endothermic peak around 50 °C disappeared and the endothermic peak appeared at around 62 °C. A comparison with results reported here appears difficult due to the different handling of the samples. Our results were obtained on samples that have been stored frozen for some months whereas those reported in the literature display postmortem changes in the muscle measured on unfrozen material.

3.2. Heating of sharks

One of the species mentioned above, the smooth-hound, was used to follow the influence of preheating the shark on DSC

Table 3
Denaturation temperatures (T_{onset}, T_{max}, °C) and denaturation enthalpy (ΔH, J g^{-1} wet weight) measured on shark muscle

Species	T_{onset}	T_{max}	ΔH	T_{onset}	T_{max}	ΔH	T_{onset}	T_{max}	ΔH
Catsharks	39.6	42.3	0.04	46.0	48.2	0.3	66.4	71.5	0.3
Smooth-hounds	41.2	43.6	0.2	48.2	50.0	0.4	68.3	72.1	0.5
Liveroil sharks	41.5	43.5	0.1	40.7	48.6	0.6	67.9	72.0	0.2

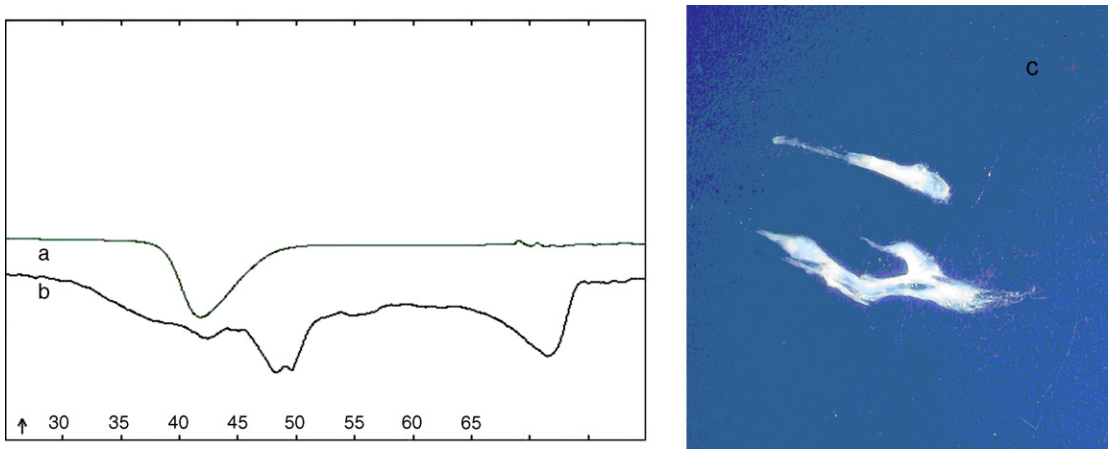

Fig. 5. Comparison of DSC curves taken on intramuscular connective tissue (a) and muscle (b) of catshark; *x*-axis, furnace temperature (°C); *y*-axis, exothermic heat flow (mW) and fibres of connective tissue dissected from whole catshark muscle (c).

Table 4
Denaturation temperatures (T_{onset}, T_{max}, °C) and denaturation enthalpy (ΔH, J g^{-1} wet weight) measured on SF and DF muscle and skin of smooth-hounds

Item	T_{onset}	T_{max}	ΔH	T_{onset}	T_{max}	ΔH
Skin, SF	44.1	47.4	13.0	–	–	–
Skin, DF	42.1	48.1	11.0	–	–	–
Muscle, SF	46.6	49.9	2.1	68.5	72.1	0.5
Muscle, DF	37.8	45.9	2.7	68.6	72.1	0.6

curves of both muscle and skin. At first, the influence of repeated freezing on the DSC curve of raw material was evaluated because it was included in the protocol of the trial. It becomes obvious that freezing for a second time in connection with further frozen storage of 2 months showed a certain influence on the DSC curves (Fig. 6 and Table 4). A second freeze in connection with further frozen storage appeared to have an effect, especially for the myosin fraction of whole muscle as can be seen by changes in both the transition temperature and transition enthalpy. What can be seen is a decrease in transition temperature accompanied by an increase in transition enthalpy which is possible caused by thaw-loss pushing up the protein content in the sample. It seems therefore recommendable in further investigation the transition enthalpy to express as J g^{-1} protein and not as J g^{-1} wet weight of sample. This increase in ΔH observed in the DF sample did not agree with reported decrease in the thermal stability of thresher shark (*Alopias pelagicus*) muscle during frozen storage at −18 °C [14]. It has further been observed that during frozen storage of silvertip shark (*Carcharhinus albimarginatus*) the exothermic peak at around 45 °C visible for both fresh and 7 days frozen stored muscle disappeared in the muscle stored longer than 14 days. The transition temperature of the endothermic peak of around 57 °C shifted to a lower temperature, and the thermal denaturation enthalpy of muscle diminished with storage time. This revealed that the thermal stability of shark muscle decreased for the duration of storage time [16]. However, these reports mentioned here did not include repeated freezing steps.

Thawed shark samples which have been heated to a given temperature and have been refrozen and frozen stored for 2 months were subjected to DSC analysis (Figs. 7 and 8 and Tables 5 and 6). In skin samples the endothermic collagen peak at about 48 °C decreased with increasing heating temperature until it disappeared completely (Fig. 7 and Table 5). At the same time, after heating at 50 °C a new peak appeared at lower temperature (about 28 °C). The new peak that appeared in samples preheated to at least at 50 °C is likely caused by gelatine which is a denaturation product of collagen [18]. With increasing temperature the denaturation enthalpy decreased almost gradually.

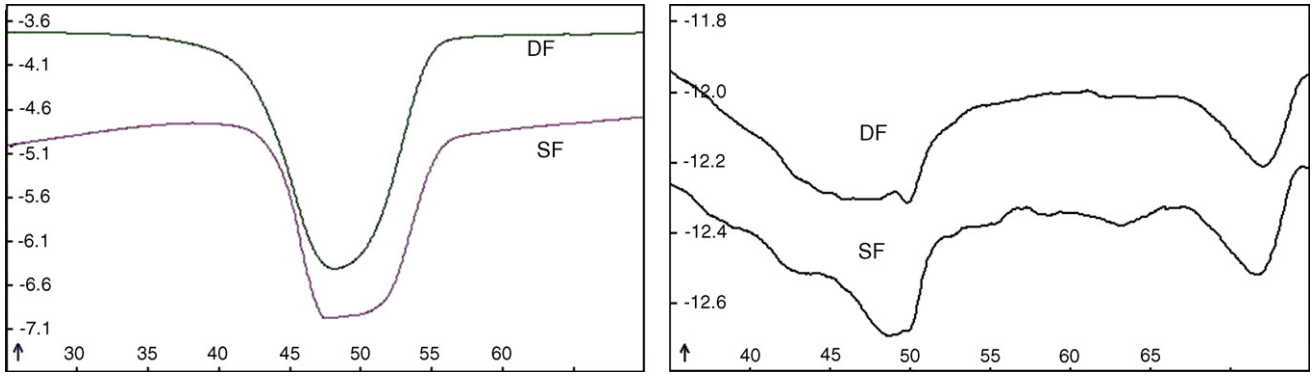

Fig. 6. DSC curves taken on single (SF) and double (DF) frozen samples of skin (left) and muscle (right) of smooth-hounds; *x*-axis, furnace temperature (°C); *y*-axis, exothermic heat flow (mW).

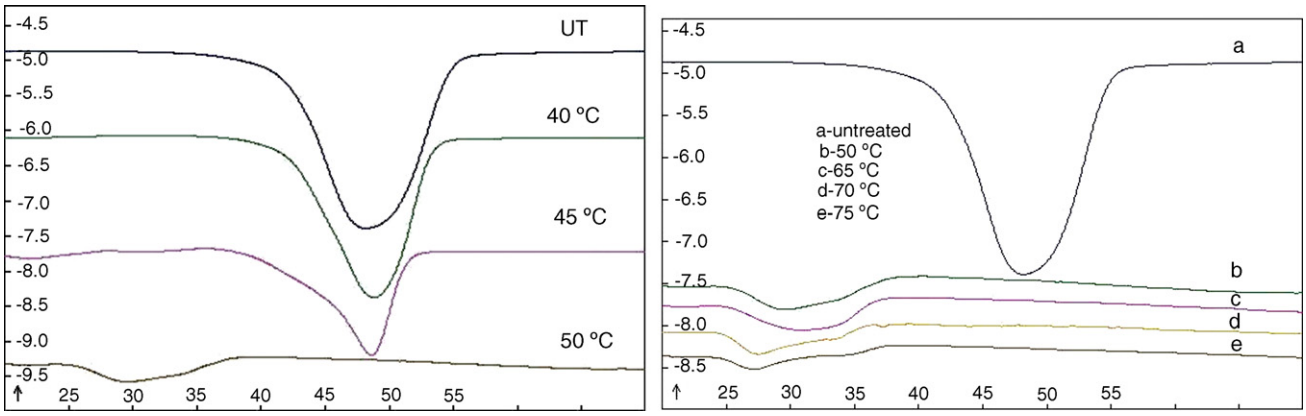

Fig. 7. DSC curves taken on preheated samples of skin of smooth-hounds dependent on heating temperature; *x*-axis, furnace temperature (°C); *y*-axis, exothermic heat flow (mW).

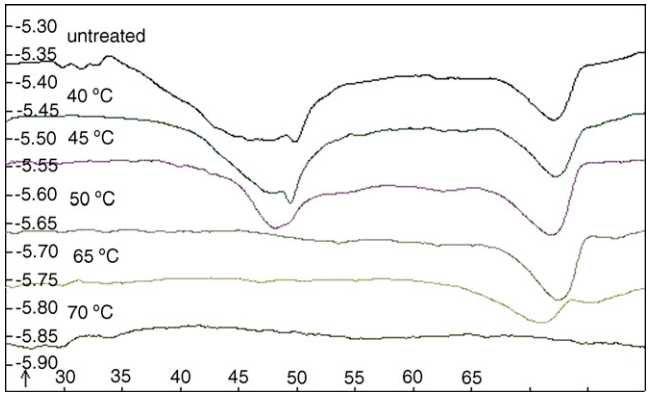

Fig. 8. DSC curves taken on preheated meat samples of smooth-hounds dependent on heating temperature; *x*-axis, furnace temperature (°C); *y*-axis, exothermic heat flow (mW).

Table 5
Denaturation temperatures (T_{onset}, T_{max}, °C) and denaturation enthalpy (ΔH, J g^{-1} wet weight) measured on preheated samples of skin of smooth-hounds dependent on heating temperature

Preheating	T_{onset}	T_{max}	ΔH
Untreated	42.1	48.1	13.0
40	42.4	48.9	10.4
45	43.6	48.6	5.0
50	25.7	29.7	0.8
65	25.2	31.3	0.9
70	24.8	27.6	0.3
75	24.6	27.3	0.2

Table 6
Denaturation temperatures (T_{onset}, T_{max}, °C) and denaturation enthalpy (ΔH, J g^{-1} wet weight) measured on preheated meat samples of smooth-hounds dependent on heating temperature

Preheating	T_{onset}	T_{max}	ΔH	T_{onset}	T_{max}	ΔH
Untreated	37.8	45.9	2.7	68.6	72.1	0.6
40	46.5	49.4	1.4	68.3	72.2	0.6
45	44.7	48.0	0.7	67.1	72.0	0.8
50	–	–	–	68.2	72.4	0.7
65	–	–	–	65.9	70.7	0.7
70	–	–	–	–	–	–

Fig. 8 displays the DSC pattern taken on shark meat and the respective transition temperatures and enthalpies are shown in Table 6. In the thermally untreated sample which is identical to the DF meat sample shown in Fig. 6 and Table 5 two endothermic peaks were clearly detectable. The first peak diminished gradually in samples preheated to 40 and 45 °C and disappeared completely in the 50 °C preheated sample. In the sample preheated to 65 °C the second peak diminished slightly and changes to lower transition temperature. In samples preheated to 70 °C the proteins appeared denatured completely. That means peaks were no longer visible. The transition enthalpy of the first peak decreased with increasing preheating temperature (Table 6). In contrast transition temperature of the first peak did not decrease until the peak disappeared. On the other hand, the second peak remained almost unchanged in transition temperature except for the 65 °C preheated sample until it disappeared completely. Some changes (increase) were observed in transition enthalpy of the second peak in samples preheated to higher temperatures. This is possibly due to the fact that ΔH was not quoted as ΔH per gram of protein in the sample. Therefore, liquid loss caused by heating (i.e. an increased protein content) is not taken into account and resulted in an apparent increase in ΔH.

Results obtained allow to follow changes in muscle proteins caused by heating the shark meat and skin. DSC pattern are strongly dependent on heat applied previously and can therefore be used as an indication of the endpoint temperature being reached during preheating.

The effects of heat on meat proteins particularly the implications on structure and quality of meat products were reviewed very recently [27]. It was pointed out that the cooking temperature where conformational changes of the proteins occur (commonly called denaturation temperature) has been mostly investigated by DSC. Its advantage is that it can be used in complex mixtures and at high concentrations of proteins, which is the situation occurring in meat. While few papers on assessment of the previous heat treatment given to meat by using DSC are available [28,29], they are almost lacking with regard to fish muscle. Sequential heating of muscle samples followed by DSC analysis can obviously be seen as another approach to study the contribution of single proteins to thermal profile. Using beef *semimembraneosus* muscle as an example, DSC curves taken

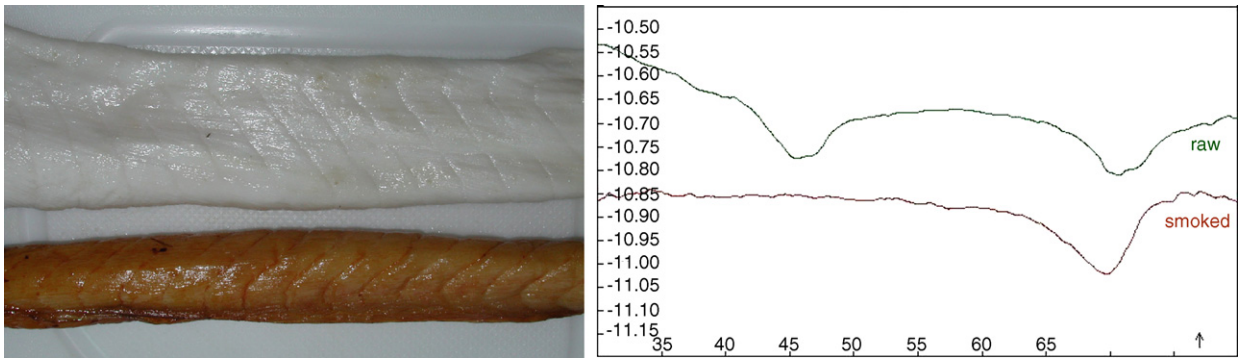

Fig. 9. (Left-hand side) Picture of frozen-thawed belly flaps (above) and "Schillerlocken" (below). (Right-hand side) DSC curves of frozen-thawed belly flaps (above) and "Schillerlocken" (below); *x*-axis, furnace temperature (°C); *y*-axis, exothermic heat flow (mW).

show the sequential elimination of the three endothermic transitions through controlled heat treatment [30,31]. On this basis cooked beef samples were related to rare, medium and well-done meat. Sequential heating of beef *M. longissimus dorsi* to nine different end temperatures of 50, 55, 60, 68, 72, 75, 80 and 85 °C, was also used by [28]. A progressive reduction in ΔH occurred as the heat treatment temperature increased. DSC curves of samples previously heat treated at 75 °C and higher temperatures were featureless, because the meat was irreversible and practically completely denatured during the earlier heat treatment. By application of multivariate regression techniques to DSC data it appeared possible to develop DSC to an automatic method for determination of previous maximum temperature heat treated beef with a prediction error of 0.6 °C in the temperature range 50–72 °C. Results confirm those previously reported [29] where it was found that heat treatment when applied to meat samples the peaks in the DSC curve gradually disappear and variations in the cooked sample pattern can be related to the previously applied treatment. Temperature and duration of heat treatment were found to be important to the degree of denaturation and therefore the DSC pattern.

Finally, an example of practical importance should be used to explain the usefulness of DSC measurements for characterisation of previously heat treatment. Probably, the best known shark product in Germany is "Schillerlocken", the smoked belly flaps of spiny dogfish. The raw material, belly flaps, are imported mostly by processors in frozen condition. After thawing and hot smoking the final product is prepared and can be sold to the consumer. In contrast to other shark species (Table 1), spiny dogfish contain an important amount of fat (31.3% in raw material and 40.6% in smoked product). Fig. 8 characterises the influence of processing on both the appearance and DSC pattern. It becomes obvious that colour differences between raw material and smoked product are enormously with a $\Delta E = 37.1$ ($L^* = 70.3$, $a^* = 0.2$, $b^* = 5.4$ and $L^* = 45.1$, $a^* = 7.6$, $b^* = 31.6$, respectively). The DSC curve taken on the raw material shows two distinct endothermic peaks with T_{max} of about 45 and 70 °C. In the smoked product, however, the low temperature peak has disappeared and only the second peaks is present. Unfortunately, from the thermal events that have been taken place on meat proteins it is only possible to conclude that smoking include a heating step up to about 50 °C. It is impossible to conclude from the DSC pattern of the hot smoked product whether a core temperature of 60 °C has been applied to the product as this temperature is demanded by the guidelines of the German Food Code. It is furthermore impossible to use DSC curves taken on skin for concluding the heat applied to the product because belly flaps are hot smoked only skinless. As shown in Fig. 9, hot-smoking influences the proteins of shark meat and causes obviously colour changes due to the quantity and composition of the smoke deposits and their interaction with the tissue components. Wood used for smoking has an important influence on colour of smoked products. It is reported that high temperature increases the deposition of higher boiling components and their polymerisation and other action with muscle components. Browning can also be caused by reaction of proteins with carbonyl products of lipid oxidation, a reaction which is more prominent in fatty fish than in lean fish muscle [32].

4. Conclusions

The Council Regulation (EC) No. 104/2000 on the common organisation of the markets in fishery and aquaculture products obliges the Member States to publish a list of the commercial designations accepted in their territory. The German list includes surprisingly 17 different shark species. Probably, consumer buy very seldom sharks as sharks are rarely subject of quality-oriented investigations in research and control, too. As a review of relevant literature indicated that information on thermal stability of shark meat and skin are comparably rare, it suggested itself within our investigation on the thermal stability of seafood to look closer on shark. Due to the low availability of shark species the work concentrated on those caught in the English channel during a research cruise. These species were characterised by their proximate composition and thermal stability of meat and skin. Differences between species were obvious but not strong. DSC pattern of shark meat showed two main endothermic peaks and additionally a smaller one at lower temperature. Skin was characterised by a pronounced peak that can be attached to collagen.

Additionally, DSC measurements were taken on previously heat-treated shark meat and skin. Peaks disappeared gradually in the DSC curves taken on meat with increasing temperature applied. In skin samples the collagen peak at around 48 °C disap-

peared completely after heating to 45–50 °C whereby after heat treatment to 50 °C a new small peak appeared at lower temperature (around 28 °C) that resulted probably due to denaturation of collagen to gelatine. Using "Schillerlocken" and the raw material used for processing (belly flaps of spiny dogfish) the influence of hot smoking on the DSC curve was demonstrated.

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