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THERMAL CHARACTERISTICS OF GELATIN EXTRACTED FROM EMPEROR (SHAARI) SKIN: EFFECTS OF ACID CONCENTRATION AND TEMPERATURE OF EXTRACTION

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ABSTRACT This study was conducted in order to evaluate the effects of acid concentration and temperature of extraction on the glass transition temperature of gelatin extracted from the skin of emperor fish. Gelatin extraction yield increased with the increase of acetic acid concentration and temperature. The onset of glass transition temperature decreased with the increase of extraction temperature up to 50 ^{o}C and then remained nearly constant, indicating that structural breakdown reached its maximum at 50^{o}C. The decrease in glass transition was more pronounced at 0.01 N compared to the 0.1 and 1.0 N samples. The increase of acid concentration during extraction shifted the curve towards lower temperature indicating increasing concentration decreased the glass transition temperature. More plasticized samples were formed with the increase of acid concentration. Unfolding temperature decreased exponentially with the increase of extraction temperature. Similar to the glass transition, the curves of unfolding temperature also shifted to lower temperature, whereas the decrease was more pronounced in the case of higher (1.0 N) concentrated samples. The extraction concentration and temperature did not show significant effect on the onset solids melting temperature.

Keywords: Fish skin gelatin, Glass transition, Solids-melting, Shaari, Amino acid.

INTRODUCTION Gelatin is a biopolymer that has very broad applications in the food, pharmaceutical and photographic industries. The quality of a gelatin for a particular application depends largely on its structural properties, as well as its physico-chemical properties that are greatly influenced not only by the species or tissue from which it is extracted, but also by the severity of the manufacturing method. The method of pretreatment and extraction greatly affects the physicochemical properties of the extracted gelatin (Montero and Gomez-Guillen, 2000). An optimization of the tissue extraction procedures and a better knowledge of the properties of fish skin gelatin could be helpful in rationalizing the use of fish processing by products. Collagen, the parental form of gelatin, is abundant in the skins and bones of animals and fish. The extraction of

gelatin from collagen involves several steps such as alkali and/or acid pretreatments for collagen hydrolysis, followed by the main extraction in water above 45 ^{o}C (Wainerwright, 1977; Montero and Gomez-Guillen, 2000). The amino acid compositions of gelatin from selected fish species are significantly different, thus functionality of selected fish gelatins, such as film forming properties may also be different (Avena-Bustillos et al. 2006). Studies indicated that warm-water fish gelatins exhibited better functional properties than cold-water fish gelatins (Muyonga et al. 2004; Avena-Bustillos et al. 2006). Cold water fish skin gelatin showed low gelling and melting temperature compared to the gelatin from warm water fish skin (Gilsenan and Ross-Murphy, 2000). Structural attributes of gelatin is related to its thermal characteristics, such as glass transition, freezing point, thermal unfolding, solids-melting, and decomposition. Thermal analysis determines different phases and states of foods as a function of water content and temperature (Rahman, 2004; Rahman, 2006). These characteristics could be visualized clearly in the state diagram when thermal characteristic temperatures are plotted as a function of solids content (Rahman, 2009).

An optimization of the tissue extraction procedures and a better knowledge of the properties of fish-skin gelatin could be helpful in rationalizing the use of fish residues (Gomez-Guillen et al. 2002). The objective of this study was to determine the effects of acid concentration and temperature of extraction solution on the thermal characteristics (glass transition, unfolding and solids-melting).

MATERIALS AND METHODS One batch of emperor (Arabic Shaari) (*Lethrinus microdon*) skin was collected in the month of August 2008 from local super market in Muscat. The skin was stored at -40 ^{o}C until used for the extraction and further analysis.

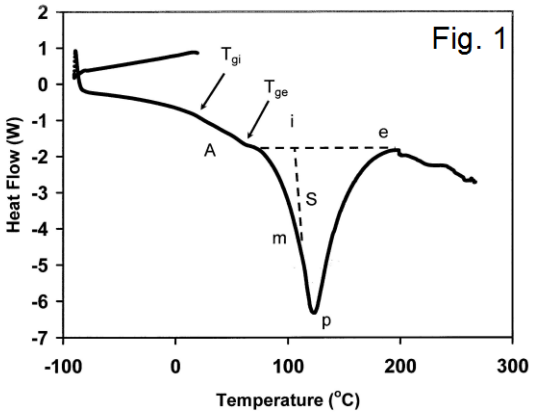
Sample preparation Commercial gelatins were bought from Sigma, Louis, OM, USA (porcine powder: catalogue number G 2500 and bovine powder: catalogue number: G 9382). Frozen skin was thawed at room temperature for about 1 hour and then the attached flesh was removed by scratching with a knife and de-scaled. Skin was washed with running tap water and then it was divided into three batches. The first batch was used for gelatin extraction. Second batch of the skin was dried in a convection oven at 80^{o}C for 18 hr. The third batch was dried in a desiccator containing silica gel at 20 ^{o}C. Both dried skin was ground into powder by a hammer mill with sieve size 1.0 mm (Model MF 10 Basic, IKA Works, USA).

Extraction procedure was carried out similarly as previously described by Gomez-Guillen and Montero (2001). The concentration and temperature of acetic acid solution were 0.01, 0.1 and 1 N, and 4, 20, 50 and 80 ^{o}C, respectively. The solution-skin mass ratio for extraction was used as 6:1.

The first set of powder samples (extracted gelatin, air-dried skin, and silica gel-dried skin) were equilibrated in desiccator maintained at 11.3% relative humidity environment by placing saturated lithium chloride solution (20 ^{o}C). This equilibration process of the first set of powder samples showed different hygroscopic characteristics with varied moisture content after equilibration. A second set of powder was thus prepared by raising the moisture content to 16.0 g/100 g sample. All samples containing water 11.3 and 16.0 g/100 g sample were stored in air tight glass bottles at -20 ^{o}C until used for analysis.

Differential Scanning Calorimetry (DSC) Unfolding, glass transition, solids-melting, and decomposition temperatures of gelatin samples at different moisture content were measured by differential scanning calorimetry (DSC Q10, TA Instruments, New Castle, DE, USA). Average and standard deviation of 5-6 replicates were obtained for each experiment.

RESULTS AND DISCUSSION The extraction yield of gelatin from raw skin varied from 1.2 to 32.1 g/100 g dry solids in the skin. The yield of extraction varied with the extraction conditions as well as the pretreatments used. Results of this study showed that in general, gelatin extraction yield increased with the increase of acetic acid concentration and extraction temperature. Yield reflects the amount of gelatin that could be extracted from the collagen and is dependent on the solubility of collagen. Very low collagen solubility, even after heat-denaturing at 80°C or even 90°C has been reported for some marine fish species and other invertebrates (Gomez-Guillen et al., 2002; Mizuta et al., 1995).



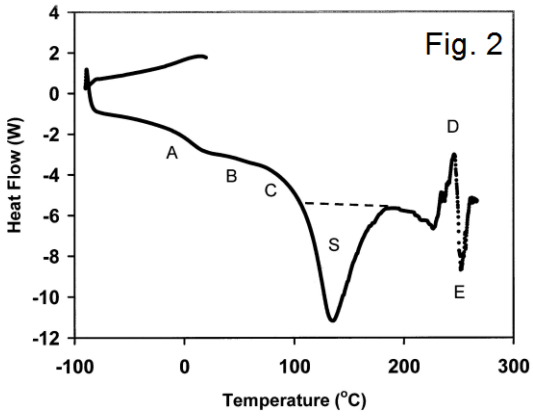


Fig. 1. DSC thermogram for air-dried shaari skin (A: glass transition, S: solids-melting, T_{gi}: onset glass transition, T_{ge}: end of glass transition; i, m, p, e: onset, maximum slope, peak and end of solids-melting)

Fig. 2. DSC thermogram for gelatin extracted from shaari skin at 1 N concentration and 4 °C (A: glass transition, B: unfolding, C: shift before solids-melting, S: solids-melting, D and E: decomposition)

The DSC thermogram for skin dried in oven and then equilibrated at water content 16.0 g/100 g sample shows a shift in the thermogrm line (marked as A) before the solids-melting endotherm (marked as S) (Figure 1).

Figure 2 shows the DSC thermogram for fish skin gelatin extracted in 1 N acetic acid at 4°C. This figure shows glass transition as a shift in the thermogram line (marked as A), a small peak as unfolding (marked as B, in some cases difficult to see over the full scale), another shift in the thermogram line before the solids-melting endotherm (marked as C), solids-melting as an endothermic peak (marked as S) and decomposition as exothermic-

endothermic peak (marked as D and E) (Figure 3). The shift before solids-melting (marked as C) was observed for 4, 20, and 50 ^{o}C, whereas 80 ^{o}C did not show the second shift before solids-melting. Two shifts in the thermogram line (marked as A and C) indicated two types of amorphous regions existed in the extracted gelatin at or below 50^{o}C.

The gelatin extracted in 0.1 N (medium concentration) at 80^{o}C also showed similar thermogram without second shift in thermogram line before solids-melting endothermic peak (Figure 3). Similar absence of the shift was also observed for 50, and 20 ^{o}C, whereas the second shift in the thermogram line was observed at 4 ^{o}C. At all temperatures, low concentration of 0.01 N showed similar thermogram without the appearance of second shift before the solids-melting. In addition, thermogram of gelatin extracted in 0.01 N and 20 or 4^{o}C showed larger clear endothermic peak as unfolding (marked as B), glass transition shift (marked as A) was merged with unfolding endothermic peak, and another the endothermic peak (marked as G) after the unfolding and before solids-melting (marked as S) (Figure 4). This indicated that less structural changes occurred in the extracted gelatin using low concentration and low temperature.

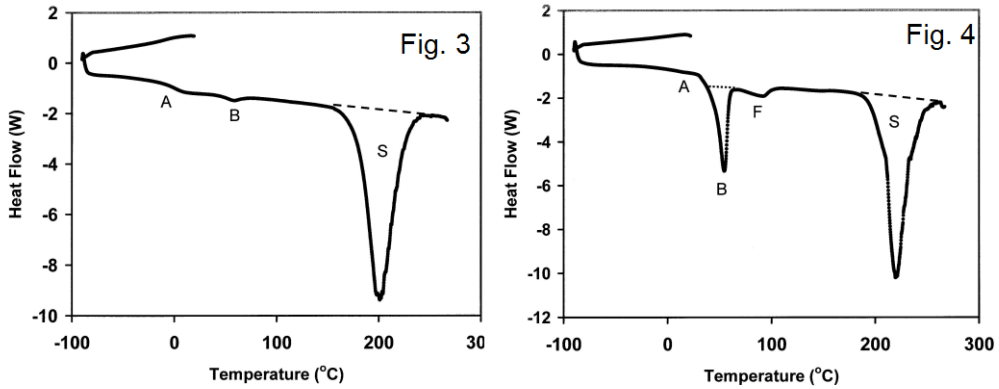


Figure 3. DSC thermogram for gelatin extracted from shaari skin at 0.1 N concentration and 80 ^{o}C (A: glass transition, B: unfolding, S: solids-melting)

Figure 4. DSC thermogram for gelatin extracted from shaari skin at 0.01 N concentration and 20 ^{o}C (A: glass transition, B: unfolding, F: endothermic peak, S: solids-melting)

The glass transition, unfolding and solids-melting characteristics of fish skin, extracted and commercial gelatin samples at moisture content 16.0 g/100 g sample were also studied. Results showed that the onset glass transition temperatures of gelatin from shaari skin decreased from 35.7 to -12.7 ^{o}C, respectively (data not shown). Rahman et al. (2008) pointed that wide variations in gelatin molecules from different sources indicated the complexity of the hydration and plasticization causing differences in the glass transition.
It was possible to develop gelatin from shaari skin with comparable onset glass transition temperature of mammalian gelatin (bovine and porcine) by selecting appropriate concentration (0.01 N acetic acid at 4 or 20^{o}C). It was mentioned in the literature that gelatin from fish skin showed lower glass transition, lower gelling point, and gel strength than mammalian gelatin (Norland, 1987; Rahman et al. 2008; Rahman and Al-Mahrouqi, 2009). It was argued in the literature that the lower thermal and mechanical

characteristics were mainly due to the lower amount of proline, hydroxyproline and glycine (Gilsenan and Ross-Murphy, 2000; Huang et al. 2004; Rahman and Al-Mahrouqi, 2009). However, the results of this study showed that the difference in thermal and mechanical characteristics of gelatin extracted from fish skin as compared to mammalian gelatin could be reduced by manipulating the extraction conditions.

Figure 5 shows that the onset glass transition temperature decreased with the increase of extraction temperature up to 50 ^{o}C and then remained nearly constant. This indicated that structural breakdown reached to maximum at 50^{o}C. Moreover the decrease in glass transition was more pronounced at 1 N concentration compared to 0.01 and 0.1 samples. The increase of acid concentration during extraction shifted the curve towards lower temperature indicating increasing concentration decreased the glass transition temperature (Figure 5). More plasticized samples were formed with the increase of acid concentration.

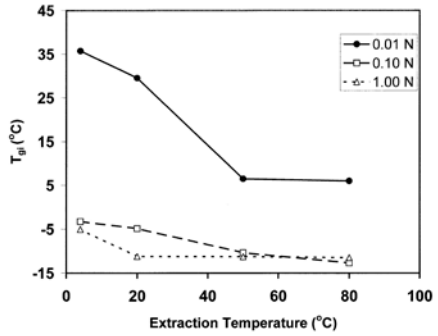


Figure 5. Onset glass transition temperature as a function of extraction temperature for different acid concentration

Similar to the glass transition, the curves of unfolding temperature also shifted to lower temperature, whereas the decrease was more pronounced in the case of higher (1.0 N) concentrated samples. The extraction concentration and temperature did not show significant effect on the onset solids-melting temperature. The value of T_{mi} was 149.0 ^{o}C compared to the 154 ^{o}C in the case of gelatin extracted from tuna skin when extraction concentration and temperature were at 0.1 N and 50 ^{o}C, respectively (Rahman et al. 2008). A generic trend could not be observed in the case of solids-melting temperature as a function of extraction temperature and concentration.

CONCLUSION The effects of acid concentration and temperature of extraction of fish gelatin on thermal characteristics (glass transition, unfolding, and solids-melting) were studied and compared to mammalian fish gelatins. Results showed that in general extraction conditions had an effect on the yield. This study showed also a difference in thermal and mechanical characteristics of gelatin extracted from fish skin as compared to mammalian gelatin. This difference could be reduced by manipulating the extraction conditions. It was possible to develop gelatin from shaari skin with comparable onset glass transition temperature of mammalian gelatin (bovine and porcine) by selecting appropriate concentration of acetic acid (i.e. 0.01 N at 4 or 20^{o}C).

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