Water Phase Transition in Pressure and Its Application in High Pressure Thawing of Agar Gel and Fish

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Abstract: Experiments were carried out with a HP differential scanning calorimeter (DSC) and a HP thawing apparatus using frozen agar gel (3%, w/w) and Atlantic salmon (Salmo salar). Small samples (0.54-0.7g) were prepared for HP calorimetric tests. Frozen samples of cylindrical agar gel (47.5mm diameter, 135mm length) and plate salmon muscle (20mm thick) were subjected to water immersion thawing (WIT) (20°C) and HP thawing at 100, 150 and 200 MPa with water (20°C). Phase transition temperature of agar gel was close to phase diagram of pure water. Melting temperature of salmon was generally lower than phase diagram of pure water probably due to the presence of solutes and cellular structures in fish. HP DSC tests demonstrated a good correlation between temperature (T) and average pressure (P): T = -1.22-0.0946P-0.000115P2 (R2=0.99, n=10). For agar gel thawing time was 50.3±2.7, 36.4±2.2 and 30.8±1.8min, or 73, 53 and 45% of WIT time (68.7±4.3min) at 100, 150 and 200 MPa, respectively. For fish thawing time was 26.6±2.1, 22.6±1.4, 18.1±1.4 and 17.0±1.3 min for WIT, HPT at above pressures, respectively.

Keywords: High pressure; phase transition; thawing; calorimeter; fish

0 Introduction

Freezing and thawing processes are important technologies for preservation of the quality of frozen foods. Retention of fresh-like quality is the primary focus of freezing preservation and expectation of consumers. Traditional freezing process is generally slow, resulting in large extra-cellular ice crystal formation, which causes texture damage, accelerates enzyme activity and increases oxidation rates (Bello, Luft & Pigott, 1982; Ngapo, Babare, Reynolds & Mawson, 1999). Thus, improvement in the freezing process is often related to increasing the freezing rate based on high efficient refrigeration systems. Thawing is generally slower than freezing, causing further damages to frozen food texture. Less attention has been paid to using novel thawing technologies to preserve the tissue structure and product quality. Indeed, due to microbial and enzyme activities, a minimal ambient temperature should be ensured for the thawing process. Rapid thawing at low temperatures can help to prevent the loss of food quality during thawing process (Okamoto & Suzuki, 2002). This is obviously a challenge for traditional thawing processes, because a lower ambient temperature results in less temperature difference between the frozen sample and the surrounding that is the main driving force for the thawing process.

Elevated pressure depresses the freezing point of water from 0ºC to -21ºC at about 210 MPa (Bridgman, 1912). This phenomenon allows a frozen sample to be thawed at temperatures as low as -21ºC (at 210 MPa). Freezing and thawing processes at high pressure are innovative processes

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with a great potential for the food industry. The decrease of freezing point under pressure significantly enlarges the temperature difference between the frozen sample and the ambience, and thus effectively increases the driving force and the rate of thawing. According to Plank's model, the freezing/thawing time is inversely proportional to the temperature difference between test sample and its ambient, (International Institute of Refrigeration, 1986). For a thawing process carried out at 20°C of ambient temperature, the conventional thawing gives a temperature difference of about 20°C, while for high-pressure thawing (HPT) at 200 MPa the difference will be approximately twice as much. Thus, theoretically HPT time at 200 MPa can be only half of conventional immersion thawing time. If the thawing is carried out at 4°C, the HPT time can be as low as one fifth of conventional thawing time because of the enlarged relative difference in temperature between the frozen sample and the ambience. Thus, HPT process offers considerable potential for rapid thawing applications.

The early research attempts to HPT process were carried out mostly in medical field. Taylor (1960) reported that a slow freezing rate followed by a HPT process at 225 MPa significantly improved the cell survival ratio of human conjunctiva. Some recent studies demonstrated the advantages of HPT process, including reduction in thawing time and preservation of food quality (Zhao, Fores & Olson, 1998; Le Bail, Chevalier, Mussa & Ghoul, 2002a; Le Bail et al., 2002b; Zhu, Ramaswamy & Simpson, 2004a; Park, Ryu, Hong & Min, 2006; Alizadeh, Chapleau, De Lamballerie & Le Bail, 2007). Makita (1992) observed that HPT process of frozen beef at 120 MPa took one-third shorter time than thawing process at 0.1MPa and produced sensory qualities comparable to those of conventional thawed products. Okamoto and Suzuki (2002) observed that there was a slight decrease of thawing loss for pork meat processed with HPT, while discoloration was not recognized with naked eyes up to 200 MPa. Park et al. (2006) demonstrated that HPT treatment effectively improved the quality of frozen pork below 100 MPa.

A HPT process involves in compression heating, pressure-dependent temperature change, phase transition, heat transfer. It is more complicated than a conventional thawing process. Understanding thermal behaviors during HPT process are important for the application of HPT technology and improvement of product quality, but available scientific information is limited (Le Bail et al., 2002a; Urrutia et al., 2007). Early high-pressure equipment frequently did not contain temperature sensors within pressure chamber. As a result, temperature changes under pressure were not reported (Ting, Balasubramaniam & Raghubeer, 2002). Nowadays temperature probes are included in pressure chamber, but it's still a challenge to monitor phase transition and pressure-temperature changes in different locations of a frozen food during a HPT treatment due to the limitation of probe flexibility. There are several studies focusing on modeling of HPT processes (Chourot, Boillereaux, Havet & Le Bail, 1997; Denys, Van Loey & Hendrickx, 2000; Ousegui, Le Bail & Havet, 2008). Chourot et al. (1997) modeled the thawing of an aqueous solution (4% NaCl) at pressures of 100-150 MPa. Denys et al., (2000) established a heat transfer model for temperature prediction during HPT processes by taking into account the pressure dependence of the latent heat of a food model called Tylose (methylcellulose gel, about 78% water content). Ousegui et al. (2008) developed a numerical model for HPT processes that was validated using Tylose slabs ($100\times100\times25mm^3$).

The objective of this work was (1) to monitor temperature and phase transformational changes in model gel (agar) and fish samples during different HPT processes, and (2) to compare/understand the difference of thawing thermal behaviors between water and fish in various HPT conditions.

1 Materials and methods

1.1 High pressure DSC test

A high-pressure (HP) differential scanning calorimeter (DSC) (Fig. 1) was used in this study. The details of the HP DSC system as well as experimental methods can be found in previous papers (Zhu, Bulut, Le Bail & Ramaswamy, 2004b; Zhu, Ramaswamy & Le Bail, 2004c). Low concentration agar gel (3%, w/w) and fresh Atlantic salmon were used in the HP DSC experiment. Agar gel was prepared as described in the following section. Salmon were obtained from a local market (Carrefour, Nantes, France). Small samples (0.54-0.7g) of these materials were prepared for HP calorimetric experiments. Each specimen was vacuum-packaged in a polyethylene bag (80 μm thick multiplayer film) (La Bovida, Nice, France). Packaged samples were stored in a cooler (4°C) before experiments. Test sample was installed in sample cell as previously described in Zhu et al. (2004b; 2004c). Air bubbles were carefully removed from the cell during sample installation by filling them with the pressure fluid. After calorimetric experiments, moisture content of each salmon sample (71.2±1.4 %) was determined by drying in a ventilated oven at 103°C for 24 h.

1.2 High-pressure thawing test

Experiments were carried out in a 4.5 L capacity cold isostatic press (Model CIP-42260, 102 mm diameter and 559 mm high, ABB Autoclave Systems, Columbus, OH) (Fig. 1). The medium used for pressure transmission in the system was distilled water containing mineral oil (2%) (ABB Autoclave Engineers, Columbus, OH). The pressure chamber was jacketed to allow circulation of temperature-controlled water for adjusting the temperature of the pressure medium.

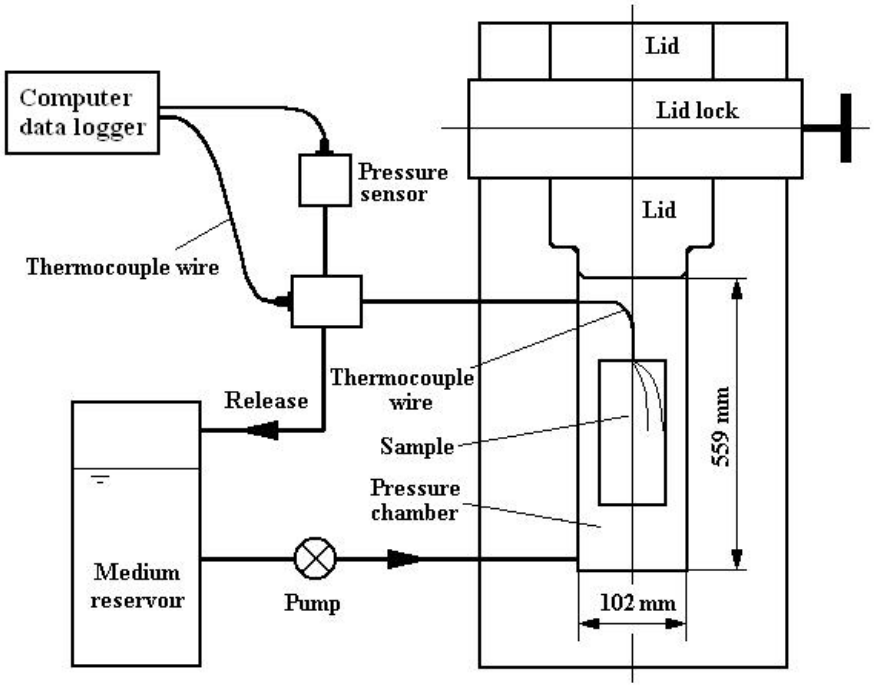

Fig. 1 Schematic description of the high-pressure experimental system.

To obtain temperature signals from test samples inside the pressure chamber, stainless steel shielded thermocouple wires (K-type, 0.5 mm in diameter, Omega, Stamford, CT) were fixed through a threaded nipple by silver welding. The pressure was measured through a pressure transducer connected on the pressure line. Temperatures and pressure were recorded using a data

logger (Agilent 34970A , Agilent Technologies Canada Inc. Mississauga, ON) during the HPT process.

Low concentration agar gel (3%, w/w) was used as a food model in this study because it had thermo-properties similar to water but its convective heat transfer was stopped due to the gel network during freezing and thawing experiment. Agar powder (Becton Dickinson, MD) and distilled water (3%, w/w) were mixed in a flask. The mixture was well mixed using a magnetic stirrer for complete dissolution at temperature close to boiling point. When cooled to about 70°C, the solution was poured into sample holder and sealed with a rubber stopper (Fig. 2) by retaining a column of 135 mm length and 47.5 mm diameter. Three K-type thermocouples (0.5 mm diameter, Omega, Stamford, CT) were in the middle region of test sample with the tip located along different radial planes: center, midway between the center and the surface (midway) and near the surface (surface) (see T_o, T_m and T_r in Fig. 2). Before the freezing treatment, the prepared samples were aged in a colder (4°C) overnight for gel texture maturity.

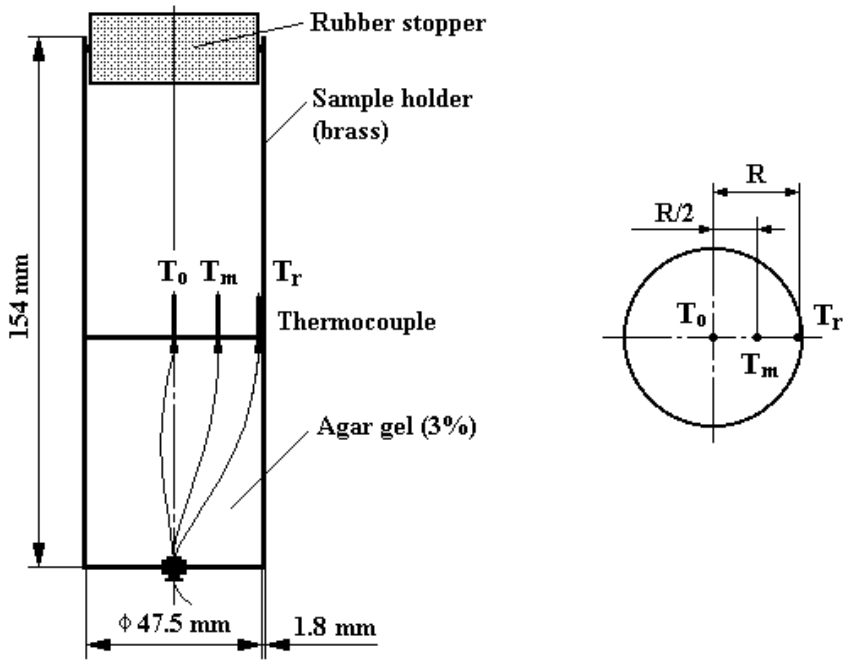

Fig. 2 Schematic description of cylindrical sample holder and thermocouple installation for freezing and high pressure thawing of agar gel.

Fresh Atlantic salmon (about 4 kg) was obtained from Waldman, a special market of fresh fish in Montreal, Canada. The consignment was procured and transported from the East Coast of Canada to Montreal by a refrigerated truck within 24 h. After de-skinning and filleting in post-rigor condition, the larger salmon pieces were cut into smaller pieces. Several plate sample holders (Fig. 3) were used for temperature monitoring during freezing and thawing processes of fish samples. A K-type thermocouple (OMEGA Eng. Stamford, CT) was placed at the geometric center of each sample holder. Fish samples were filled into the holders with same shape and size (45.2±0.6g), thus resulting in comparable temperature readings. After sampling, the holders were vacuum-sealed using the same polyethylene pouch (Fig. 3) as mentioned above and ice-stored until freezing process.

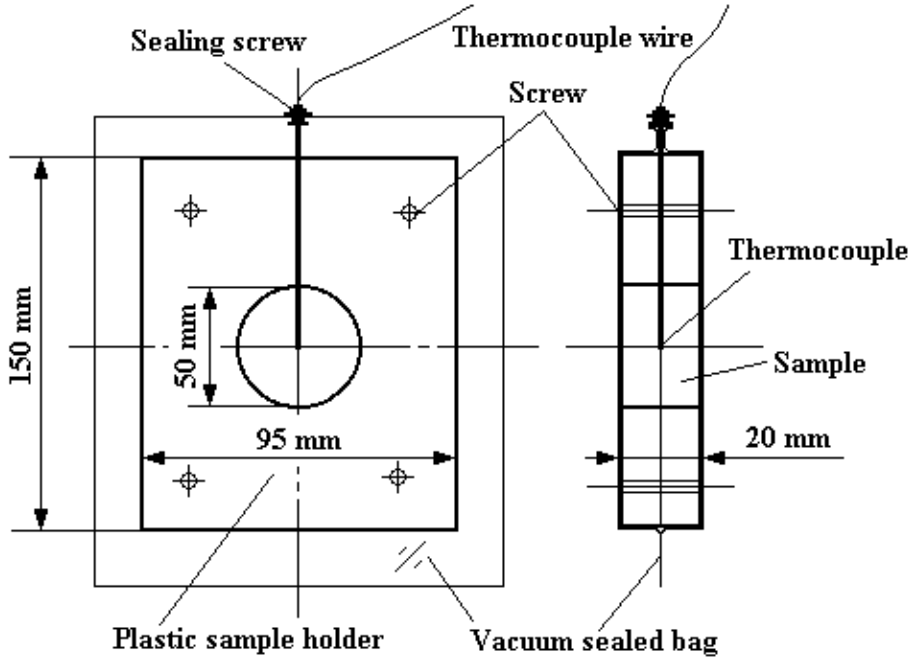

Fig. 3 Schematic description of the sample holder and thermocouple installation for monitoring temperature during freezing and high-pressure thawing processes of fish.

The all samples were frozen in a conventional air freezer (about -30 ºC). Three pressure levels (100, 150 and 200 MPa) were applied for HPT treatments. The temperature of the pressure medium was maintained close to 20°C during the HPT tests. When the temperature at the sample center reached 10°C, the pressure was released and samples were taken out from the pressure chamber. For comparison, water immersion thawing (WIT) tests were performed using a water tank (about 60 L) at 20ºC. During WIT tests, frozen samples were directly immersed in the water tanks without forced agitation. The thawing was completed when the sample temperature reached 10ºC.

2 Results and discussion

2.1 High pressure DSC test

For each pressure-scan test, a pressure-dependent endothermic calorimetric peak was obtained. Fig. 4 demonstrates the endothermic peaks of heat flow rate against pressure observed with fresh salmon muscle at different temperatures as well as agar gel at -10°C. For the same type of sample, pressure-scan at lower temperatures resulted in the peak summit to appear at higher pressures. Compared with that of agar gel, the thermogram of salmon had (1) smaller peak area, (2) lower onset pressure, (3) lower pressure at peak summit, and (4) larger peak span. The area of a peak represents the melting latent heat of ice in the frozen sample tested. Salmon contained less water content undergoing phase transition, and thus the peak area appeared much smaller than that of agar gel (Fig. 4). The presence of solutes in salmon is expected to depress the phase change point (either temperature or pressure). This should be the main reason why the pressure at peak summit for salmon was much lower than that for agar gel at -10°C (Fig. 4). Concentration/dilution phenomenon of solutes in salmon during freezing/thawing causes further changes in phase transition behavior and hence the widening of the peak-span as compared to the peak of agar gel (Fig. 4).

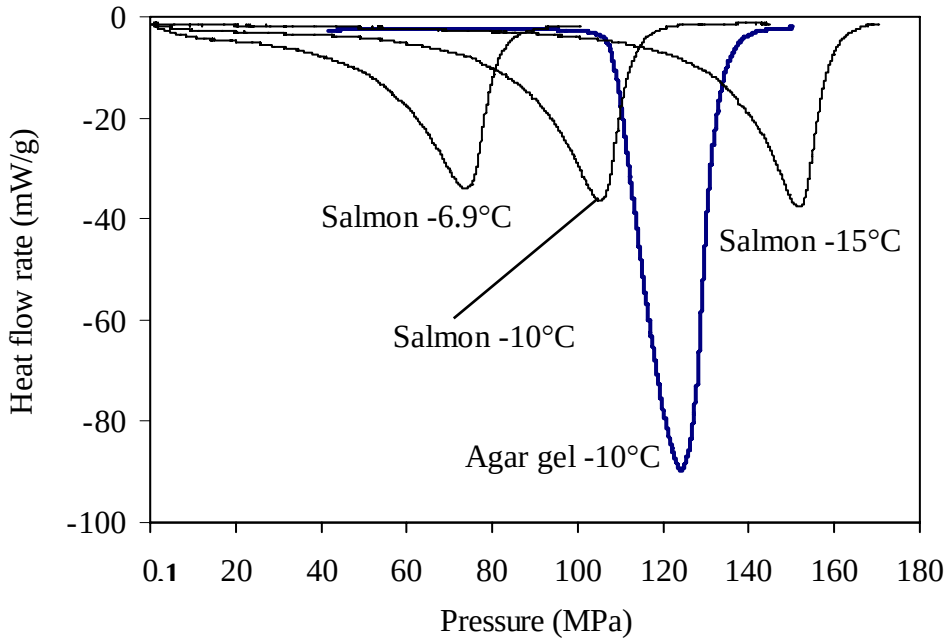

Fig. 4 Thawing heat flow rate during pressure-scan (0.3MPa/min) tests at different calorimetric temperature for frozen samples of salmon muscle and agar gel.

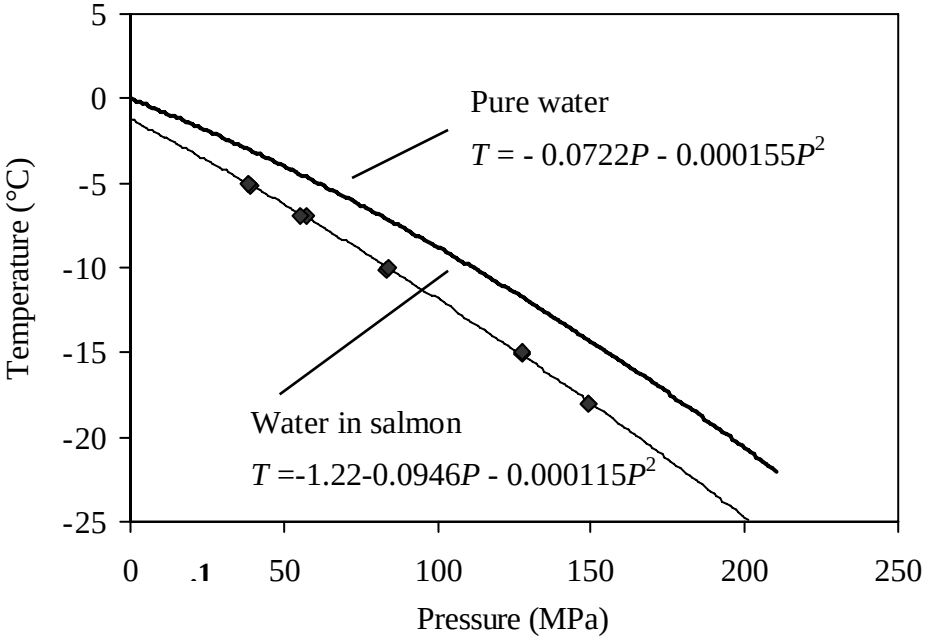

Fig. 5 Phase transition comparison between water in salmon and pure water (Bridgman 1912).

The onset and summit of the pressure-scan endothermic peak is related to the start and end of ice melting, respectively (Le Bail et al. 2002b). An average pressure was calculated over the peak as in Zhu et al. (2004b). Fig. 5 shows the results of phase transition observed in salmon. Regression analysis indicated a good relationship between temperature and average pressure:

T =-1.22-0.0946P - 0.000115P^2 (R^2 =0.99, n=10) (1)

Based on the average pressure, phase transition point in salmon was significantly (P<0.05, df = 1/10) lower than that of pure water (Fig. 5). For example, the average pressure of phase transition at -5, -6.9, -10, -15 and -18°C was 38.7, 56.2, 83.7, 127.8 and 149.3 MPa for salmon, as compared to 61.2, 81.4, 111.7, 155.7 and 179.9 MPa for pure water, respectively. Alternately,

the phase transition temperature at 100, 150 and 200 MPa was -11.8, -18 and -24.7 for salmon, much lower than that of -8.8, -14.4 and -20.5°C for pure water, respectively. No significant difference was observed for the phase transition between agar gel and water.

2.2 Thawing of agar gel

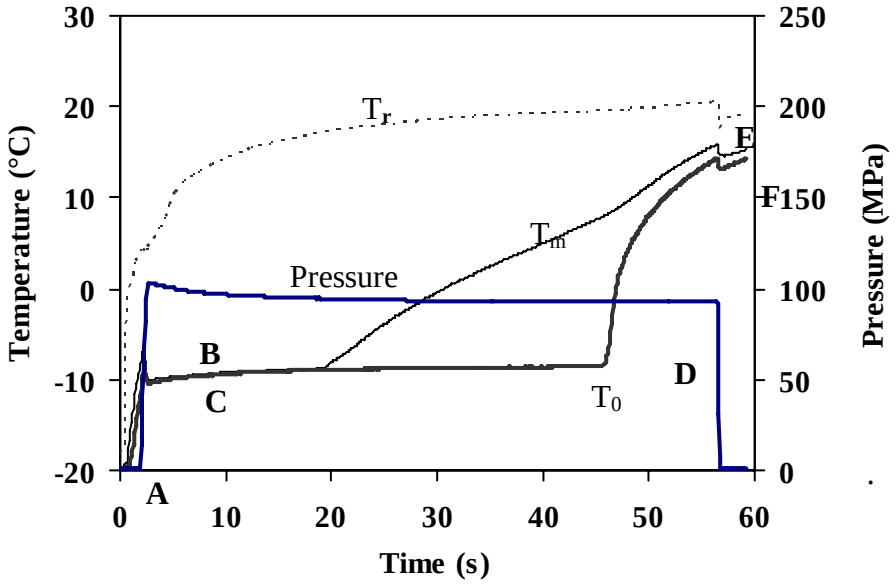

Fig. 6 Temperatures at different radial position of a cylindrical agar gel sample during high-pressure thawing at 100 MPa (medium at 20°C).

Fig. 6 shows a typical example of changes in pressure and temperature at different radial locations during HPT process at 100 MPa. Temperatures rose rapidly during sample installation (about 2 min) before pressurization (particularly near the surface) (AB in Fig. 6) due to immersion of the frozen sample in pressure medium (about 20°C). Pressure increase caused a decrease in temperature inside the sample just following the pressure-depressed phase diagram (Bridgman, 1912) (BC in Fig. 6). Then there was a melting plateau of temperature at middle way (17 min) and center (about 43 min) (CD in Fig. 6). The surface temperature didn't demonstrate a plateau due to fast heating by the medium. The temperature plateau showed a slight increase (from -10.3 to -8.5°C) because of the pressure decrease (from 102.8 to 92.5 MPa) caused by the volume decreasing of the sample during the phase change from ice to water. When melting was completed, central temperature rose quickly (DE in Fig. 6). Pressure was released when sample temperature reached at a high level. This caused an instantaneous cooling of the sample and pressure medium due to the effect of adiabatic expansion (EF in Fig. 6).

Fig. 7 plots temperature profiles at the center of test samples subjected to water immersion thawing (0.1MPa, 20°C) and HPT process at 100, 150 and 200MPa (20°C). The melting temperature was -0.8°C for water immersion thawing, and -10.3°C (103MPa) to -8.5°C (92.5MPa), -15.4°C (152MPa) to -13.5°C (138MPa) and -21.1°C (202MPa) to -19.1°C (186.2MPa) (Fig. 7), slightly lower than phase diagram of pure ice-water (Bridgman, 1912) (Fig. 8) probably due to the presence of agar in these samples. The melting plateau of central temperature lasted about 43.1±3.2, 30.4±2.0 and 22.5±1.7 min for thawing treatments at 100, 150 and 200 MPa, respectively, with significant differences between each other ($P < 0.05$) (Table 1).

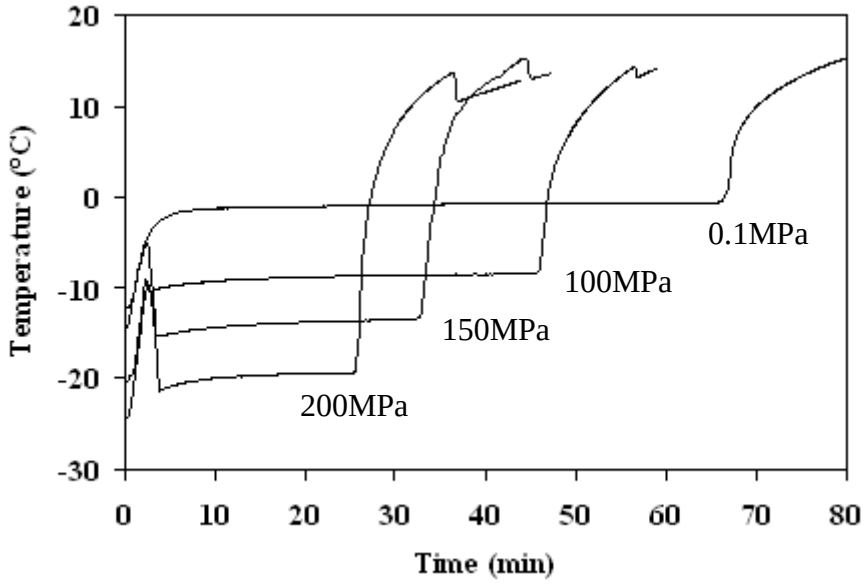

Fig. 7 Temperatures at center of cylindrical agar gel samples during water immersion thawing under different pressures (medium at 20 °C).

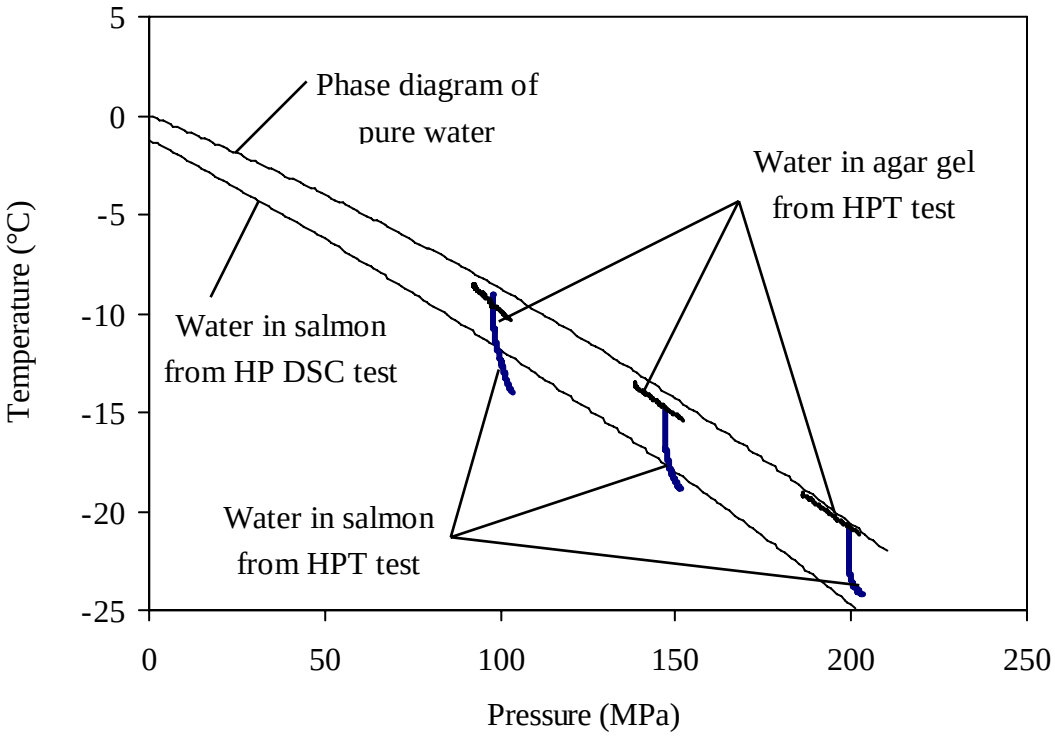

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Fig. 8 Phase transition of water in salmon and and agar gel observed from high pressure thawing tests as compared to that from high-pressure DSC tests and reference data for pure water (Bridgman 1912).

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Tab.1 The melting and total thawing process time (min) (mean±S.D., n=3).

Thawing condition	Agar gel sample		Fish sample	
	Melting	Total process	Melting	Total process
WIT (0.1MPa, 20°C)	59.7±4.1 a	68.7±4.3 a	19.2±2.0 a	26.6±2.1 a
100MPa (20°C)	43.1±3.2 b	50.3±2.7 b	12.8±1.7 b	22.6±1.4 b
150MPa (20°C)	30.4±2.0 c	36.4±2.2 c	10.5±1.4 c	18.1±1.4 c
200MPa (20°C)	22.5±1.7 d	30.8±1.8 d	8.5±1.1 d	17.0±1.3 c

The final criterion temperature for calculating thawing time was 2.5ºC for WIT (water immersion thawing) at 4ºC and 8ºC for all other treatments. Different letters (a, b, c, d) in each column indicate significant difference ($P < 0.05$, $df = 1/6$) between these thawing processes.

In order for calculating the thawing time, assuming the initial time for HPT process was at the time when a sample was immersed into medium and the final time was that when temperature reached at 8ºC. For HPT treatments at 0.1, 100, 150 and 200 MPa, the thawing time was 68.7±4.3, 50.3±2.7, 36.4±2.2 and 30.8±1.8min (Table 1), or the ratio was 1.0, 0.73, 0.53 and 0.45 respectively. According to Plank's model for freezing/thawing, the ratio of HPT to WIT time at medium temperature of 20°C would be about 0.69, 0.58 and 0.49 for HPT at 100, 150 and 200 MPa, respectively. The observed data were close to the predicated values of Plank's model.

2.3 Thawing of fish

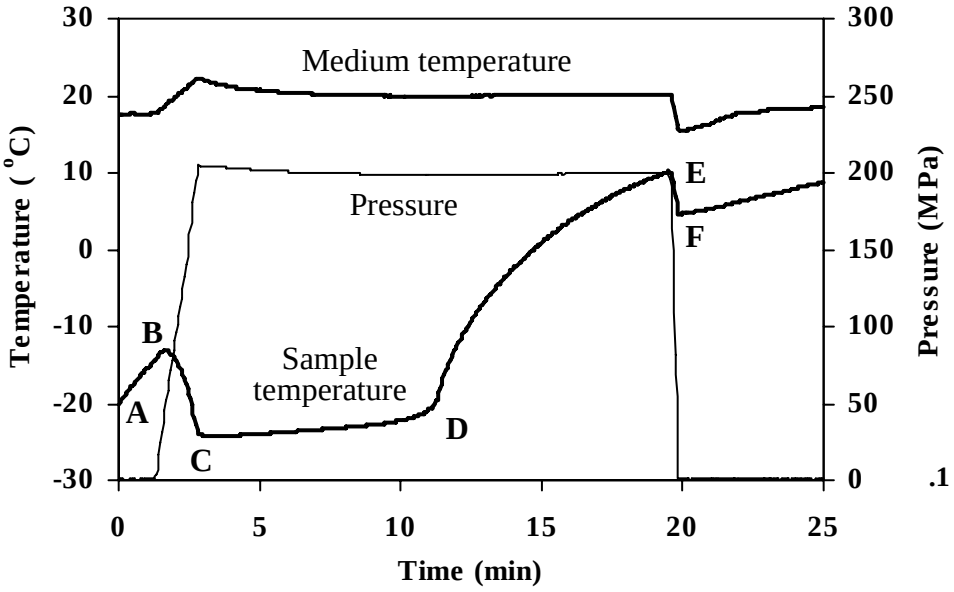

Fig. 9 Pressure and central temperature of fish sample during high-pressure thawing process at 200 MPa.

Fig. 9 is an example of the pressure and temperature changes during HPT process at 200 MPa. Temperature increased slightly during the period of sample preparation (about 2 min) before pressurization (AB in Fig. 9) due to the temperature difference between the sample and the medium in pressure chamber. Pressurization caused a slight increase in medium temperature, but sample temperature dripped to the level corresponding to the pressure depressed melting point (BC in Fig. 9) that was lower than the phase transition temperature of pure water (Fig. 8) (Bridgman, 1912). The melting temperature increased from -24.5 to -21°C (pressure decreased from 204.1 MPa to 199.1MPa) (CD in Fig. 9). When thawing was completed, sample temperature rose quickly (DE in Fig. 9). During the depressurization, the sample and the pressure medium were instantaneously cooled (EF in Fig. 9) because of the positive coefficient of thermal expansion of water. To avoid ice crystal formation due to adiabatic cooling, sample temperature must be brought to a minimum level above 0°C before releasing pressure. For

thawing time calculation of HPT process, the final temperature before pressure release was selected as 8°C in this study.

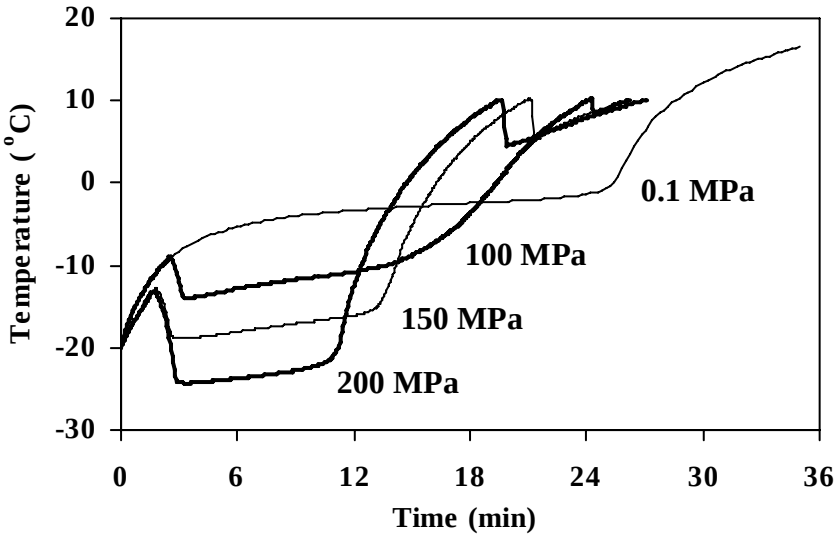

Fig. 10 Temperatures at the centers of fish samples during the thawing processes at different pressure levels with medium temperature of 20°C.

Fig. 10 shows different temperature profiles of fish samples subjected to WIT (0.1 MPa) and HPT processes at 100, 150 and 200 MPa. A higher pressure resulted in a lower plateau of ice melting temperature. Melting temperature increased from -13.9°C (103MPa) to -9°C (97.8MPa), -18.9°C (152MPa) to -15.1°C (147MPa) and -24.5°C (203MPa) to -21°C (199MPa). This means the melting point of fish samples under pressure was much lower than those of agar gel samples (Fig. 8), especially at beginning of thawing. The difference in depression of melting point between fish and agar gel samples could be related to the presence of solutes and cellular structures in fish samples (28.8% dry matter) that would shift the phase diagram towards lower melting point (ice I). The melting temperature plateau lasted 12.8±1.7, 10.5±1.4 and 8.5±1.1 min for HPT processes at 100, 150 and 200 MPa, respectively (Table 1).

The depression of melting point increased the temperature difference between the sample and the pressurization medium during HPT process. As a result, HPT time was significantly reduced as compared to WIT (Fig. 10 and Table 1). A higher pressure resulted in a shorter thawing process, but the thawing time difference between 150 and 200 MPa was not significant ($P > 0.05$), as compared with that between 100 and 150 MPa (Table 1). According to Plank's model for freezing/thawing, the HPT/WIT time ratio at 20°C would be about 0.69, 0.58 and 0.49 for HPT at 100, 150 and 200 MPa, respectively. The observed values were 0.85, 0.68 and 0.64 for HPT at 100, 150 and 200 MPa, respectively (Table 1), higher than the theoretical values, because the actual HPT times included sample installation, pressurization and post-thawing temperature rise (see AB, BC and DE in Fig. 9, respectively) that took almost half of the whole HPT treatment for the small samples tested.

3 Conclusions

The phase transition of water under pressure and HPT experiments were investigated using HP DSC and HP thawing for frozen agar gel and salmon fish. Following observations were obtained:

I The melting temperature of frozen samples of low concentration agar gel was close to that of

pure ice-water phase diagram under high pressure.

II For frozen salmon, the temperature plateau during melting appeared an increasing trend, i.e., -13.9 to -9°C, -18.9 to -15.1°C and -24.5 to -21°C at 100, 150 and 200 MPa, respectively, which was much lower than that of agar gel samples due to the presence of solutes and cellular structures in fish samples.

III High pressure caused a depression of the ice-melting temperature during thawing, thus significantly accelerated the thawing process. The thawing time was 68.7±4.3, 50.3±2.7, 36.4±2.2, 30.8±1.8min for frozen agar gel cylinders, and 26.6±2.1, 2.6±1.4, 18.1±1.4, 17.0±1.3 min for fish plates tested at 0.1, 100, 150 and 200 MPa (20°C), respectively.

Acknowledgements

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水在高压下的相变及其在琼脂凝胶和鲑鱼肉高压解冻中的应用

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摘要：本实验采用高压差示扫描热量计和高压解冻装置处理冷冻的琼脂凝胶（3%，w/w）和大西洋鲑鱼。用于高压量热的样品量约 0.54-0.7g。将冷冻的柱状琼脂凝胶（47.5mm 直径，135mm 高度）和片状鲑鱼肉（20mm 厚度）进行水浸泡解冻（WIT）（20℃）和高压解冻（100、150、200MPa，20℃水）。琼脂凝胶中的相变温度与纯水的相变图接近。鲑鱼的溶解温度普遍比纯水的相变图低，可能是因为溶质和细胞结构的存在。高压差示扫描热量计测定结果表示，温度（T）和平均压力（P）之间存在很好的相关性: T=-1.22-0.0946P-0.000115P2（R2=0.99，n=10）。在 100、150、200MPa 高压下，琼脂凝胶的解冻时间分别是 50.3 ± 2.7，36.4 ± 2.2，30.8 ± 1.8min，是水浸没解冻时间（68.7 ± 4.3min）的 73、53 和 45%。鲑鱼肉解冻的时间分别是 26.6 ± 2.1（WIT），22.6 ± 1.4（100MPa），18.1 ± 1.4（150MPa）和 17.0 ± 1.3min（200MPa）。

关键词：高压；相变；解冻；量热；鱼

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