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Freezing / Thawing and Cooking of Fish

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1. Introduction

One of the greatest challenges for food technologists is to maintain the quality of food products for an extended period. Fish and shellfish are perishable and, as a result of a complex series of chemical, physical, bacteriological, and histological changes occurring in muscle, easily spoiled after harvesting. These interrelated processes are usually accompanied by the gradual loss or development of different compounds that affect fish quality. Fresh seafood has a high commercial value for preservation, and the sensory and nutritional loss in conventionally frozen/thawed fish is a big concern for producers and consumers. This chapter present the effect of Freezing/Thawing and Cooking on the quality of fish.

2. Freezing

Freezing is a much preferred technique to preserve food for long period of time. It permits to preserve the flavour and the nutritional properties of foods better than storage above the initial freezing temperature. It also has the advantage of minimizing microbial or enzymatic activity. The freezing process is governed by heat and mass transfers. The concentration of the aqueous phase present in the cell will increase when extra ice crystal will appear. This phenomenon induces water diffusion from surrounding locations. Of course, intra cellular ice induces also an increase of the concentration of the intra cellular aqueous phase. The size and location of ice crystals are considered most important factors affecting the textural quality of frozen food (Martino et al., 1998). It has been recognized that the freezing rate is critical to the nucleation and growth of ice crystals. Nucleation is an activated process driven by the degree of supercooling (the difference between the ambient temperature and that of the solid-liquid equilibrium). In traditional freezing methods, ice crystals are formed by a stress-inducing ice front moving from surface to centre of food samples. Due to the limited conductive heat transfer in foods, the driving force of supercooling for nucleation is small and hence the associated low freezing rates. Thus, the traditional freezing process is generally slow, resulting in large extracellular ice crystal formations (Fennema et al., 1973; Bello et al., 1982; Alizadeh et al., 2007a), which cause texture damage, accelerate enzyme activity and increase oxidation rates during storage and after thawing.

Pressure shift freezing (PSF) has been investigated as an alternative method to the existing freezing processes. The PSF process is based on the principle of water-ice phase transition under pressure: Elevated pressure depresses the freezing point of water from 0°C to -21°C at about 210 MPa (Bridgman, 1912). The sample is cooled under pressure to a temperature just above the melting temperature of ice at this pressure. Pressure is then fast released resulting

in supercooling, which enhanced instantaneous and homogeneous nucleation throughout the cooled sample (Kalichevsky et al., 1995). Ice crystal growth is then achieved at atmospheric pressure in a conventional freezer. Pressure shift freezing (PSF), as a new technique, is increasingly receiving attention in recent years because of its potential benefits for improving the quality of frozen food (Cheftel et al., 2002; Le Bail et al., 2002). PSF process has been demonstrated to produce fine and uniform ice crystals thus reducing ice-crystal related textural damage to frozen products (Chevalier et al., 2001; Zhu et al., 2003; Otero et al., 2000; Alizadeh et al., 2007a). From a point of view of the tissue damage, pressure shift freezing seemed to be beneficial, causing a very smaller cell deformation than the classic freezing process.

2.1 Freezing process

Freezing is the process of removing sensible and latent heat in order to lower product temperature generally to -18 °C or below (Delgado & Sun, 2001; Li & Sun, 2002). Figure 1 shows a typical freezing curve for the air blast freezing (ABF). The initial freezing point was about -1.5 °C and was observable at the beginning of the freezing plateau (Alizadeh et al., 2007a). The temperature dropped slowly at follow because of the water to ice transition. This freezing point depression has been classically observed in several freezing trials (not always) and has been recognized to be due to the presence of solutes and microscopic cavities in the food matrix (Pham, 1987). The nominal freezing time was used to evaluate the freezing time. The nominal freezing time is defined by the International Institute of Refrigeration as the time needed to decrease the temperature of the thermal centre to 10 °C below the initial freezing point (Institut International du Froid, 1986).
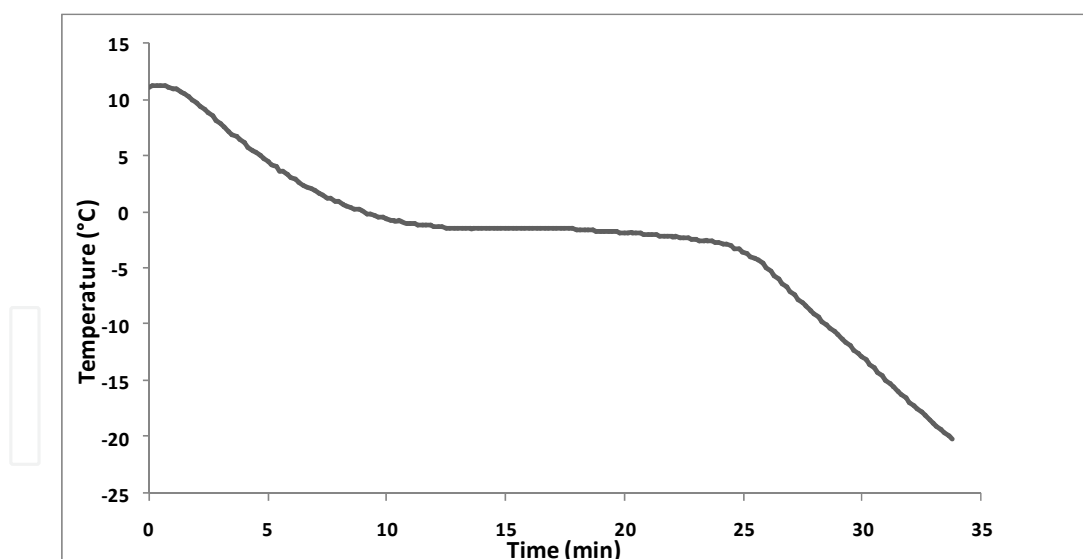

Fig. 1. A typical freezing curve of Atlantic salmon fillets obtained in air-blast freezing (Alizadeh, 2007).

Figure 2 shows a typical Pressure shift freezing curve. The process began when the unfrozen fish sample was placed in the high-pressure vessel. The temperature appeared to drop a little bit and a slight initiation of freezing can be detected at the surface of the sample after the sample was immersed into the ethanol/water medium (-18 °C) of the refrigerated bath (Alizadeh et al., 2007a). Pressurization (200 MPa) induced a temperature increase due to the

adiabatic heat generated. It took about 57 min for the sample to be cooled to -18 °C without freezing which is close to the liquid-ice I equilibrium temperature (Bridgman, 1912).
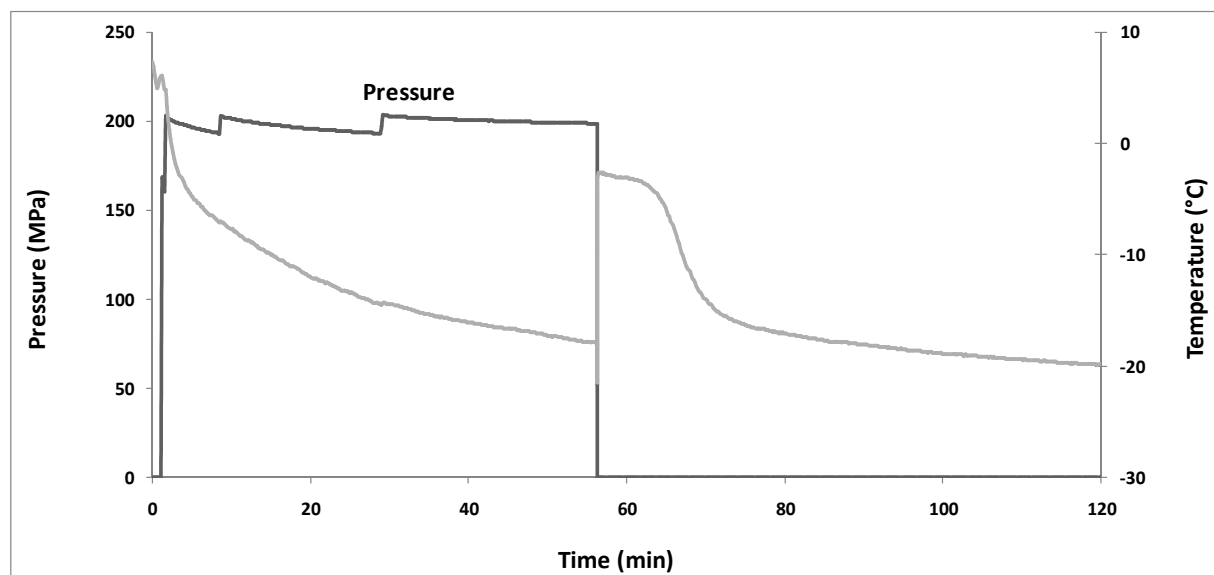

Fig. 2. A typical Pressure shift freezing curve of Atlantic salmon fillets (Alizadeh, 2007).

Then, the quick release of pressure created a large supercooling, causing a rapid and uniform nucleation, due to the shift in the freezing point back to the normal (-1.5°C) and the rapid conversion of the sensible heat (from -18 to -1.5 °C) to the latent heat. After depressurization, the temperature reached a stable temperature (-1.5 °C) for freezing at atmospheric pressure because of the latent heat release. The final step of the PSF process was similar to conventional freezing at atmospheric pressure.

2.2 Fish microstructure during freezing

Ice crystallization strongly affects the structure of tissue foods, which in turn damages the palatable attributes and consumer acceptance of the frozen products. The extent of these damages is a function of the size and location of the crystals formed and therefore depends on freezing rate. It is mentioned that slow freezing treatments usually cause texture damage to real foods due to the large and extracellular ice crystals formed (Fennema et al., 1973). Clearly, most area was occupied with the cross-section of the ice crystals larger than the muscle fibers. This means that the muscle tissue was seriously deformed after the air blast freezing at low freezing rate (1, 62 cm/h) which may cause an important shrinkage of the cells and formation of large extracellular ice crystals but it was very difficult to determine if these ice crystals were intra or extra-cellular (Figure 3). On the other hand, the intra and extracellular ice crystal have been seen during air blast freezing at high freezing rate (2, 51 cm/h). It is possible to observe the muscle fibers and analyse the size of intracellular ice crystal (Alizadeh, 2007).

The pressure shift freezing (PSF) process created smaller and more uniform ice crystals. A higher degree of supercooling should be expected during the pressure shift freezing experiments because of the rapid depressurization and the smaller ice crystals observed in the samples frozen by PSF at higher pressure. Burke et al. (1975) reported that there was a 10-fold increase in the rate of ice nucleation for each °C of supercooling. Thus, a higher

pressure and lower temperature resulted in more intensive nucleation and formation of a larger number of small ice crystals. Moreover, PSF at a higher pressure is carried out at lower temperature, creating a larger temperature difference between the sample and the surrounding for final freezing completion after depressurization. This could also be a major factor affecting the final ice-crystal size in the PSF samples. Micrographs in Figure 3 also show well isotropic spread of ice crystals in the fish tissues, especially for the 200 MPa treatments. This is because the isostatic property of pressure allows isotropic supercooling and homogeneous ice nucleation. It is quite clear that the muscle fibers in the PSF treated samples (Figure 3) were well kept as compared with their original structures. Therefore, conventional freezing problems like tissue deformation and cell shrinkage could be much reduced or avoided using PSF process (Martino et al., 1998; Chevalier et al., 2000; Zhu et al., 2003; Sequeira Munoz et al., 2005; Alizadeh et al., 2007a).
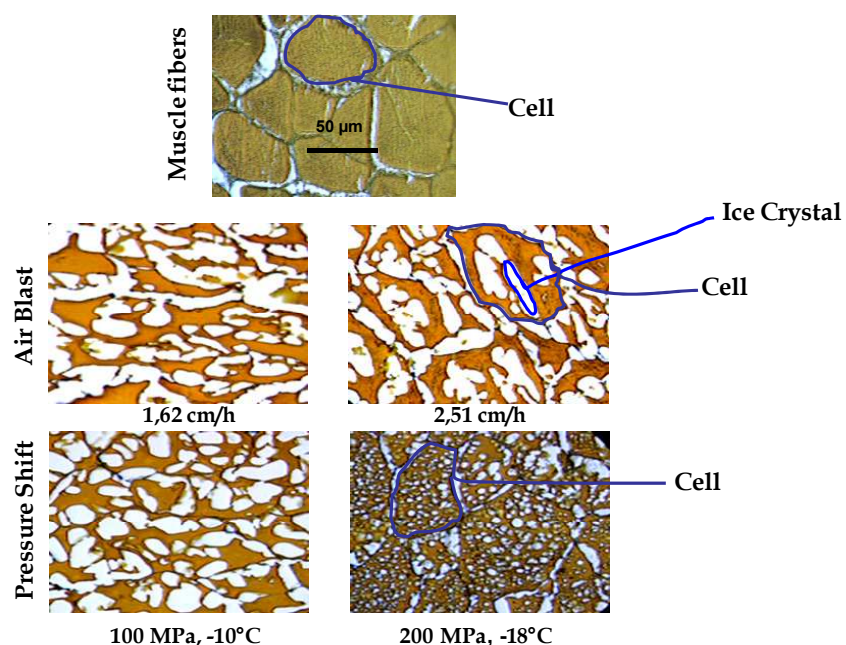

Fig. 3. Ice crystals formed in Atlantic salmon tissues during freezing (Alizadeh, 2007).

2.3 Ice crystal evolution during frozen storage

The evolution of the size of the ice crystal is important during frozen storage. It is difficult to evaluate the extracellular ice crystal for air blast freezing. But the size of high freezing rate extracellular ice crystals is smaller than low freezing rate ones. Alizadeh et al. (2007a) reported that the evolution of the intracellular ice crystal is not significant (P<0.05) during 6 months of storage for the air-blast (-30 °C, 4 m/s) and pressure (100 MPa) shift freezing. But for pressure shift freezing (200 MPa), the ice crystal size is changed after 6 months storage. Theoretically during frozen storage, small ice crystals have a tendency to melt and to aggregate to larger ones. It is known that the smallest ice crystals are the most unstable during storage. Indeed, the theory of ice nucleation permits to calculate the free energy of ice crystals as the sum of a surface free energy and of a volume free energy. The volume free energy increases faster than the surface free energy with increasing radius, explaining why the smaller ice crystals are more unstable. Thus the size of the ice crystals for pressure shift freezing (200 MPa) was stable for the first 3 months and then the size of the ice crystals

tended to coarsen for longer storage (up to 6 months). In comparison, the size of the ice crystals obtained by pressure (100 MPa) shift freezing were much stable in size, demonstrating that a high pressure level is not necessarily required when prolonged frozen storage duration is envisaged (Alizadeh et al., 2007a).

3. Thawing process

The methodology and technique used for freezing and thawing processes play an important role in the preservation of the quality of frozen foods. Conventional thawing generally occurs more slowly than freezing, potentially causing further damages to frozen food texture. The thawing rate during conventional thawing processes is controlled by two main parameters outside the product: the surface heat transfer coefficient and the surrounding medium temperature. This medium temperature is supposed to remain below 15 °C during thawing, to prevent development of a microbial flora. The heat transfer coefficient then stays as the only parameter affecting the thawing rate at atmospheric pressure. Hence, the small temperature difference between the initial freezing point and room temperature does not allow high thawing rates (Chourot et al., 1996). Figure 4 shows a typical air blast thawing (ABT) curve. The temperature augmented to reach the melting point and temperature plateau appeared during this process.
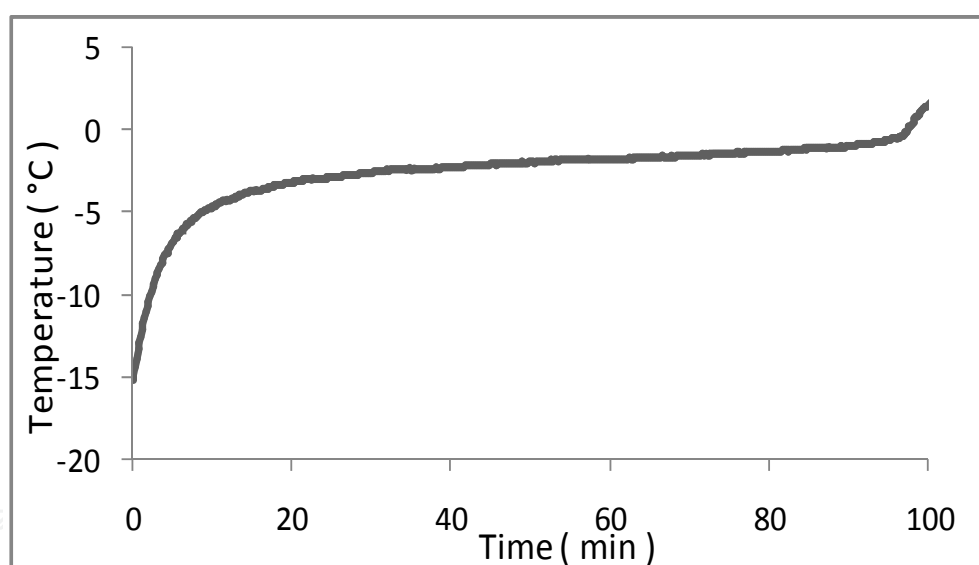

Fig. 4. A typical thawing curve of Atlantic salmon fillets obtained in air-blast thawing (Alizadeh, 2007).

Rapid thawing at low temperatures can help to prevent the loss of food quality during thawing process (Okamoto and Suzuki, 2002). This is obviously a challenge for traditional thawing processes, because the use of lower temperatures reduces the temperature difference between the frozen sample and the ambient, which is the principal driving force for the thawing process.

Pressure assisted thawing (PAT) may be attractive in comparison to conventional thawing when the quality and freshness are of primary importance. Figure 5 shows a typical pressure assisted thawing curve. Temperature increased slightly during the period of sample preparation (about 4 min) before pressurization due to the temperature difference

between the sample and the medium in pressure chamber. During pressurisation the temperature decreases according to the depression of the ice-water transition under pressure (Bridgman, 1912). Then there was a temperature plateau due to the large amount latent heat needed for melting. The temperature rose quickly when thawing was completed. During the depressurization, the sample and the pressure medium were instantaneously cooled 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 (Cheftel et al., 2000).
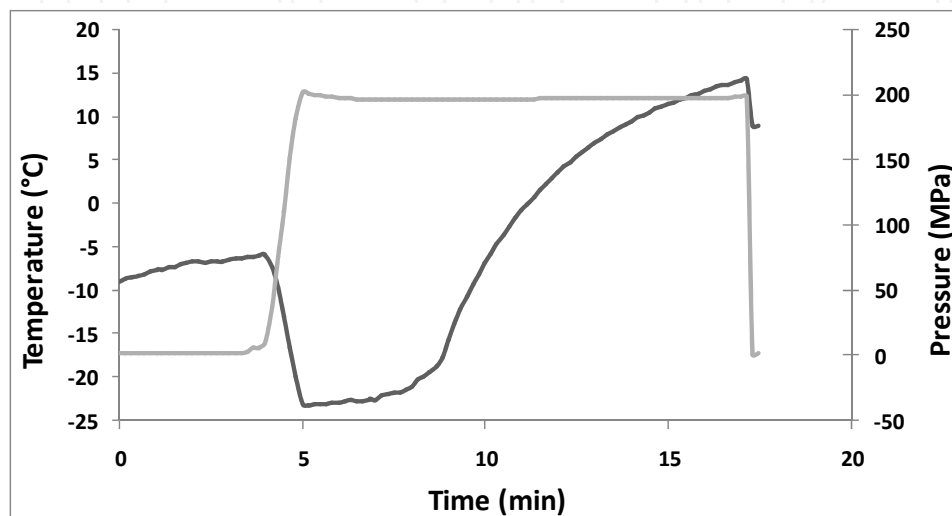

Fig. 5. A typical Pressure assisted thawing curve of Atlantic salmon fillets (Alizadeh, 2007).

3.1 Texture quality

Texture is an important quality parameter of the fish flesh. It is an important characteristic for consumer and also an important attribute for the mechanical processing of fillets by the fish food Industries. One critical quality factor influenced by freezing is food texture. Many foods are thawed from the frozen state and eaten directly, or cooked before consumption. In some cases, the texture of the thawed material is close to that of the fresh and unfrozen food. In other cases, the texture may be changed by the freezing process and yet result in a thawed product that is still acceptable to consumers. The texture of fish is modified after freezing and thawing (Figure 6). Pressure generally caused an increase in the toughness in comparison to conventional freezing and thawing (Chevalier et al., 2000; Zhu et al., 2004; Alizadeh et al., 2007b). This increase was attributed to the denaturation of proteins caused by high pressure processing. On the other hand, high pressure process was deleterious in some other aspects, mainly related to the effect of pressure on protein structures: high-pressure treatment (200 MPa) of Atlantic salmon muscle produced a partial denaturation with aggregation and insolubilization of the myosin (Alizadeh et al., 2007b). Freezing process is an important factor affecting textural quality of the fish. It is interesting to note that pressure shift freezing (200 MPa, -18 °C) induced formation of smaller and more regular ice crystals compared with air blast freezing (Chevalier et al., 2000; Alizadeh et al., 2007a; Martino et al., 1998). A tentative explanation could be that pressure shift freezing were less subjected to ice crystals injuries. Injuries involve a release of proteases (calpains and cathepsins) which are able to hydrolyse myofibrillar proteins and then to lead to quick textural changes (Jiang, 2000).
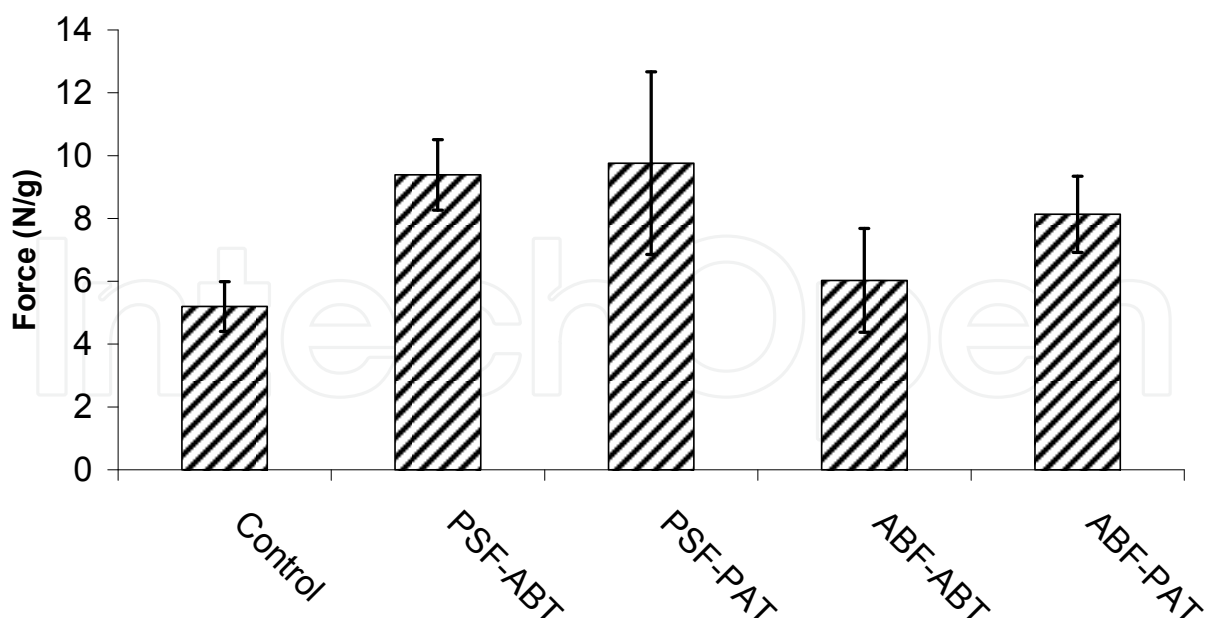
Fig. 6. Effect of Freezing (PSF, ABF) and thawing (PAT, ABT) on the texture of Atlantic salmon fillets (Alizadeh, 2007).

3.2 Colour changes

The first quality judgement made by a consumer on a food at the point of sale is its visual appearance. Appearance analyses of foods (colour and texture) are used in maintenance of food quality throughout and at the end of processing. Colour is one of the most important appearance attribute of food materials, since it influences consumer acceptability (Saenz et al., 1993).Various factors are responsible for the loss of colour during processing of food products. These include non-enzymatic and enzymatic browning and process conditions such as pH, acidity, packaging material and duration and temperature of storage.

The colour of fish is changed after freezing and thawing processes. This changes (assessed by very high colour differences ΔE) can be seen mainly caused by a strong increase in lightness (L*) and decrease for both redness (a*) and yellowness (b*) after pressure shift freezing. But this is opposite of those obtained for air blast freezing after thawing (Alizadeh et al., 2007b). Colour modifications and particularly modifications of lightness could be consequences of protein modifications. Changes in myofibrillar and sarcoplasmic proteins due to pressure could induce meat surface changes and consequently colour modifications (Ledward, 1998). The thawing process had little impact on overall colour change in fish after pressure shift freezing. But the discolouration of the flesh was visible with naked eyes after pressure assisted thawing (Alizadeh et al., 2007b). Murakami et al. (1992) also reported that an increase in all colour values (L*, a*, b*) of tuna when thawed by high pressure (50-150 MPa). This increase was stronger with increasing pressure. Furthermore, colour changes seem to be influenced by temperature, as lower temperatures caused stronger changes under the same pressure.

3.3 Drip loss

Drip loss is not only disadvantageous economically but can give rise to an unpleasant appearance and also involves loss of soluble nutrients. Drip loss during thawing is caused

by irreversible damage during the freezing, storage (recrystallization), and thawing process (Pham & Mawson, 1997). Freezing can be considered as a dehydration process in which frozen water is removed from the original location in the product to form ice crystals. During thawing, the tissue may not reabsorb the melted ice crystals fully to the water content it had before freezing. This leads to undesirable release of exudate (drip loss) and toughness of texture in the thawed muscle (Mackie, 1993). Slow freezing produces larger extracellular ice crystals and resulting in more tissue damage and thawing loss. Thus, low freezing rate (air blast freezing) resulted in more drip than high freezing rate (pressure shift freezing) (Alizadeh et al., 2007b; Chevalier et al., 1999; Ngapo et al., 1999).

As shown in Figure 7, the freezing process was generally much more important than thawing for drip loss. Drip loss was reduced for all pressure shift freezing process irrespective to the thawing process but the air blast freezing resulted in a higher drip loss.
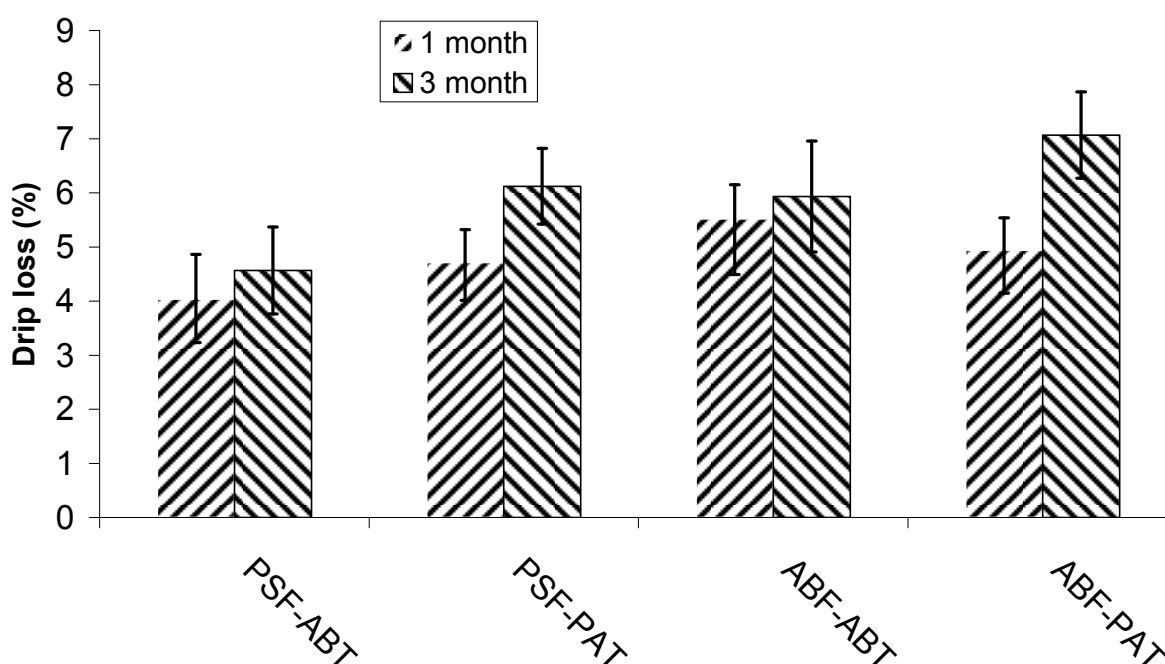

Fig. 7. Effect of Freezing (PSF, ABF) and thawing (PAT, ABT) on the drip loss of Atlantic salmon fillets (Alizadeh, 2007).

The pressure assisted thawing reduced the drip volume after conventional freezing. It can be assumed that during a slow thawing process, (corresponding to atmospheric pressure thawing), crystal accretion might occur leading to a mechanical damage of the cell membrane while thawing, and consequently in an increase of the drip volume. Pressure assisted thawing (PAT) reduced the thawing time and thus might have minimized the phenomenon of crystal accretion (Alizadeh et al., 2007b).

Few studies have reported the application of high pressure technology process for fish. Murakami et al. (1992) observed drip loss reduction in high pressure technology treated tuna meat. Chevalier et al. (1999) found that high freezing rate or high pressurization rate reduced thawing drip loss of whiting fillets (*Gadus merlangus*), but drip loss was reduced only by prolonging holding time of pressure as compared to atmospheric pressure thawing. Rouillé et al. (2002) found that high pressure technology processing (100, 150 and 200 MPa)

of Spiny dogfish (*Squalus acanthias*) significantly reduced drip loss when compared with atmospheric thawing.

Crystal growth might enhance shrinkage of muscle fibers and even disrupt the cellular structure, resulting in a greater drip loss during frozen storage. Storage temperatures should be below -18 °C for optimum quality. Some studies suggest that drip loss may increase during extended frozen storage (Alizadeh et al., 2007b; Awonorin & Ayoade, 1992). Finally, drip loss seems to be a complicated process, and more studies are necessary for better understanding the phenomenon related to drip formation during pressure assisted thawing process.

4. Cooking process

Thermal processing techniques are widely used to improve eating quality and safety of food products, and to extend the shelf life of the products. Cooking is a heating process to alter the eating quality of foods and to destroy microorganisms and enzymes for food safety. Sous vide is a French term that means under vacuum. Sous vide involves the cooking of fish inside a hermetically sealed vacuum package. Cooking under vacuum (sous vide technology) defines those foods that are cooked in stable containers and stored in refrigeration. Because these products are processed at low temperatures (65 to 95 °C), the sensorial and nutritional characteristics are maximized in comparison with the sterilized products. The final product is not sterile and its shelf life depends on the applied thermal treatment and storage temperature. Figure 8 shows a typical cooking (Water bath) curve. The cooking was finished when the temperature reached at +80°C, then put in the ice water at 0°C for cooling.
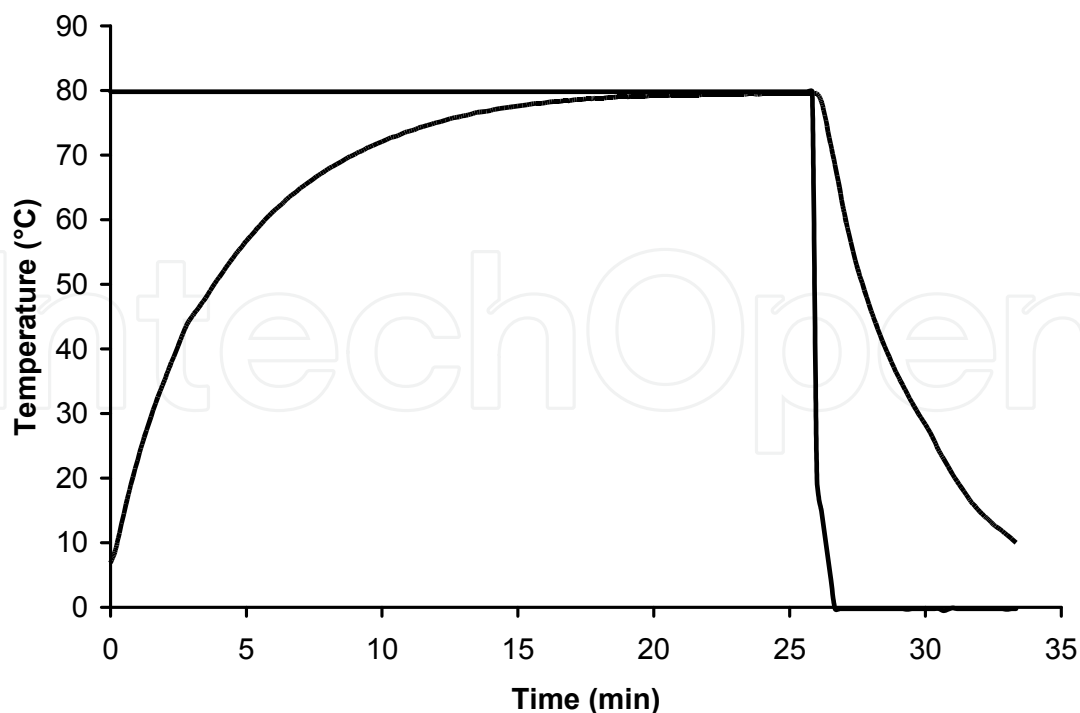

Fig. 8. Curve time/temperature during cooking under vacuum of Atlantic salmon fillets (Alizadeh, 2007).

Shaevel (1993) reported that the sous-vide process can also be used for cooking meat: this entails vacuum sealing the meat portions in plastic pouches, cooking in hot water vats for up to 4 h followed by rapid cooling at 1°C. Cooking time varied from food to food due to variation in heat transfer rates and the size of the food pieces.

4.1 Texture quality

Change in food texture was associated with heat treatment of the food such as cooking. It has been shown that thermal conditions (internal temperature) during meat cooking have a significant effect on all the meat texture profile parameters (cohesiveness, springiness, chewiness, hardness, elasticity). These reach their optimum level in the 70–80 °C range. As observed by Palka and Daun (1999), increasing the temperature to 100 °C causes the meat structure to become more compact due to a significant decrease in fiber diameter. During heating, at varying temperatures (37–75 °C), meat proteins denature and cause structural changes such as transversal and longitudinal shrinkage of muscle fibers and connective tissue shrinkage. Another effect is the destruction of cell membranes and the aggregation of sarcoplasmic proteins (Offer, 1984).

Pressure shift freezing (PSF) and cooking have an important effect on the quality of texture. Cooking process has more effect on texture than pressure shift freezing (Alizadeh et al., 2009). Meanwhile, the pressure shift freezing minimized the drip loss after cooking process. A partial cooking is a favorable fact for the pressure shift freezing, taking into account that a high proportion of fish is exposure to a cooking process before consuming. High cooking temperature can shorten cooking time and hence processing period, but it also causes high cooking loss and lower texture quality.

4.2 Protein denaturation

Denaturation can be defined as a loss of functionality caused by changes in the protein structure due to the disruption of chemical bonds and by secondary interactions with other constituents (Sikorski et al., 1976). Structural and spatial alterations can cause a range of textural and functional changes, such as the development of toughness, loss of protein solubility, loss of emulsifying capacity, and loss of water holding capacity (Miller et al., 1980; Awad et al., 1969; Dyer, 1951). In general during fish heating, sarcoplasmic and myofibrillar proteins are coagulated and denatured. The extent of these changes depends on the temperature and time and affects the yields and final quality of the fishery product.

Differential scanning calorimetry (DSC) can also be used to investigate the thermal stability of proteins and to estimate the cooking temperature of the seafood products. The proteins of salmon are denaturated after freezing and cooking processes (Figure 9). Principal peaks are corresponding to myosin (42,5°C), sarcoplasmic proteins (55,5°C), collagen (64°C) and actin (73°C) (Schubring, 1999). Alizadeh et al. (2009) found that a partial denaturation of proteins, mainly to myofibrillar proteins denaturation, is induced by pressure shift freezing, similar to the effect of pressure on protein structures: high-pressure treatment (200 MPa) of sea bass muscle (Urrutia et al., 2007). As shown in Figure 9, cooking process was caused a total denaturation of proteins as comparison with pressure shift freezing. Bower (1987) showed the proteins were completely denaturated under cooking process at 80°C.
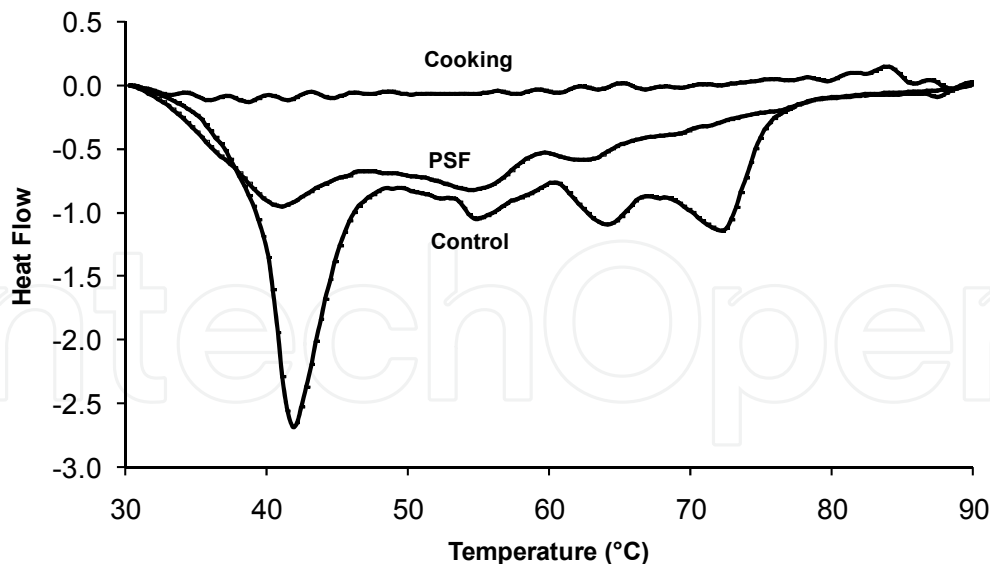
Fig. 9. Typical DSC thermograms of Atlantic salmon fillets (Alizadeh, 2007).

5. Conclusion

The quality of frozen foods is closely related to the size and distribution of ice crystals. Existence of large ice crystals within the frozen food tissue could result in mechanical damage, drip loss, and thus reduction in product quality. This chapter offers once again the advantage of pressure shift freezing process, which is widely used in the industry. Pressure shift freezing (200 MPa) process produced a large amount of small and regular intracellular ice crystals that can improved the microstructure of ice crystals (size, formation and location). The pressure shift freezing was responsible of a partial protein denaturation, which is reflected by an increase in texture. The total change of colour was observed after the freezing / thawing and cooking processes. The integration of results showed that the pressure shift freezing provides an interesting alternative compared to conventional freezing.

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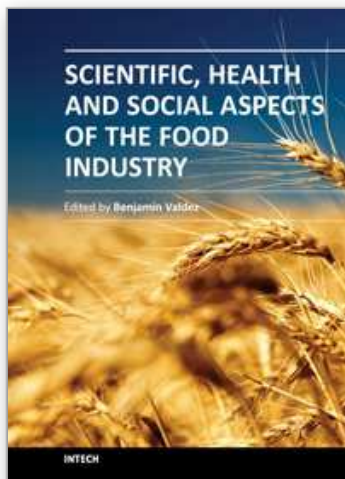
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This book presents the wisdom, knowledge and expertise of the food industry that ensures the supply of food to maintain the health, comfort, and wellbeing of humankind. The global food industry has the largest market: the world population of seven billion people. The book pioneers life-saving innovations and assists in the fight against world hunger and food shortages that threaten human essentials such as water and energy supply. Floods, droughts, fires, storms, climate change, global warming and greenhouse gas emissions can be devastating, altering the environment and, ultimately, the production of foods. Experts from industry and academia, as well as food producers, designers of food processing equipment, and corrosion practitioners have written special chapters for this rich compendium based on their encyclopedic knowledge and practical experience. This is a multi-authored book. The writers, who come from diverse areas of food science and technology, enrich this volume by presenting different approaches and orientations.

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