




Freezing and storage on aquatic food: underlying mechanisms and implications on quality deterioration

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Abstract

Fresh aquatic products have high nutritional value, but they are easily susceptible to spoilage. Freezing as an effective preservation method could better retain the quality and safety of aquatic products. However, mechanical damage caused by ice crystals and the oxidation of proteins and lipids would inevitably bring about a reduction in the quality of the frozen product during freezing and preservation. This work summarized the important factors that affected the quality of frozen aquatic products, revealed the mechanism of deterioration of frozen aquatic products on the quality through sensory evaluation and changes in physiochemical indicators. In the context of high-quality development, some improvements in frozen fish preservation were proposed to provide theoretical basis and solutions to improve the quality and efficiency of fish processing.

Keywords: freezing; aquatic products; quality; physiochemical indicators; preservation methods.

Practical Application: Aquatic food processing and regulation.

1 Introduction

In 2020, the total output of aquatic products in China was as high as 6,569.02 million tons, an increase of 1.06% over the previous year. The annual output of aquatic products in the country steadily exceeded 60 million tons from 2016 to 2020 (China Fishery Bureau, 2021). Aquatic products are widely popular among consumers because of their high nutritional value. However, due to the high water, protein, and unsaturated lipids content in aquatic products, it is susceptible to microorganisms and endogenous enzymes, which leads to a decrease in freshness and high susceptibility to deterioration and spoilage (Shi et al., 2018). This inevitably causes waste of aquatic resources, greatly increases the economic cost of aquatic products, and hinders the healthy development of the aquatic industry.

Freezing has the characteristics of high safety and application suitable for the circulation of most fish products in the market. When the low temperature method below 0 °C (-40 °C ~ -4 °C) is applied to aquatic products, it can better inhibit microbial growth and reproduction (Coombs et al., 2017), endogenous enzyme activity and its physiological and biochemical reactions (Bao et al., 2021), which is conducive to the extension of shelf life as well as long-distance transportation and long-term storage (Maqbool et al., 2021). It was found that the formation of ice crystals in aquatic products under low temperature freezing could seriously affect the integrity of its tissue cells and affected the size and distribution of ice crystals in aquatic products. Due to the long-term freezing, transportation, storage and freeze-thaw process, a series of ice crystal damage, protein oxidation, lipids

oxidation and other quality deterioration still occur in aquatic products, which has the important impact on the quality of aquatic products. Ice crystals, formed in freezing process, crystals are aggregated to form large ice crystals, causing the average size increased (Qian et al., 2022a), the number of nuclei decreased, and the total surface free energy of the crystals decreased, which also is called the phenomenon of recrystallization (Vicent et al., 2019). Therefore, how to control the recrystallization of ice crystals, inhibit the growth of ice crystals, and delay the deterioration of aquatic product quality is the key research direction of frozen preservation.

This review analyzed the factors affecting the quality of aquatic products during freezing and frozen, further discussed the mechanism of quality deterioration and proposed new methods for improvement. The purpose is to provide theoretical basis and solutions for the quality research of frozen aquatic products during transportation and storage, so as to meet the quality and efficiency improvement of aquatic product processing under the background of high-quality development.

2 The influence of freezing conditions on the quality of frozen aquatic products

2.1 Freezing temperature

The morphological characteristics of ice crystals is one of the criteria for quality assessment of frozen foods. Large and irregular extracellular ice crystals could damage the muscle

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tissue, thus affecting the quality of long-term frozen aquatic products. As the freezing temperature decreases, the generation time of the maximum ice crystal band is shortened, reducing the number of large size ice crystals (Chen et al., 2019a). The effects of

different freezing temperatures on the quality of aquatic products were listed in Table 1. It was found that the lower the freezing temperature, the smaller the changes in physiochemical properties of proteins, which could affect the water-holding capacity and

Table 1. Effects of different freezing temperatures on the quality of aquatic products.

Freezing temperature	Food	Conclusion	References
-20, -35, -40, -45, -60 °C	tuna	No increase in metMb% was observed in samples stored at -45 °C and -60 °C, and less drip loss was observed in samples stored at temperatures below -40 °C; tuna samples stored at -60 °C and -40 °C had higher color scores than those stored at -20 °C. Hardness and flavor scores showed similar trends to color.	Nakazawa et al. (2020)
-20, -40, -80 °C	<i>Larimichthys crocea</i>	The color changed the most at -20 °C, while the hardness, adhesiveness, chewiness and repulsive properties decreased, and the elasticity increased and then decreased. The malondialdehyde content (MDA) increased, and the total antioxidant capacity, superoxide dismutase activity and glutathione peroxidase activity decreased significantly, while the antioxidant indexes changed at the slowest rate at -80 °C.	Li & Sang (2015)
-18, -40, -80 °C	<i>Micropterus salmoides</i>	As the storage temperature increased from -80 °C to -18 °C, the temperature-dependent relationship held: the number of ice crystals in frozen samples gradually increased, Ca ²⁺ -ATPase activity and total sulfhydryl content of myofibrillar protein decreased significantly in frozen samples, shear force and salt-soluble protein content of perch tissues decreased significantly, while moisture content increased.	Shi et al. (2018)
-20, -30, -40, -60 °C	<i>Cyprinus carpio</i>	Drip, steaming and centrifugal losses as well as cohesiveness and chewiness were virtually unchanged at -60 °C storage. Moisture loss and texture changes were similar at -30 and -40 °C storage, but these losses were less than at -20 °C. In addition, adenosine monophosphate deaminase (AMPD) and acid phosphatase (ACP) remained active in fish during frozen storage. ATP degradation was faster at -20 °C than at -30 and -40 °C, as reflected by the change in K values. Overall, degradation of ATP still occurred at -20, -40 °C, while it was almost inhibited during storage at -60 °C.	Li et al. (2019)
-20, -30, -40 °C	<i>Siniperca chuatsi</i>	The pH, Ca ²⁺ -ATPase activity and total sulfhydryl content of <i>Siniperca chuatsi</i> muscle showed a decreasing trend at different freezing temperatures, while the surface hydrophobicity index and TVB-N showed an increasing trend; meanwhile, the lower the freezing temperature, the smaller the decrease in hardness, elasticity and chewiness of the samples; <i>Siniperca chuatsi</i> samples frozen at -40 °C had a higher α -helix content and their protein denaturation was less, while those frozen at -20 °C showed an increase in protein disorder. The protein disorder of the samples frozen at -20 °C increased significantly.	Chai et al. (2020)
-20, -30 °C	hoki and saithe	A definite loss of long-chain n-3 PUFA was observed in both saithe and hoki, light and dark muscle after 18 months of frozen storage, with greater losses observed in the samples stored at -20 °C Hydroperoxide formation was slightly more pronounced in the samples stored at -20 °C compared to -30 °C, both the saithe and the hoki dark muscle samples stored at -20 °C were significantly more rancid in flavour and odour after the 18 months period than their respective samples stored at -30 °C.	Karlsdottir et al. (2014)
-20, -30, -40, -50 °C	<i>Euphausia superba</i>	The quality of Antarctic krill frozen at -20 °C changed rapidly and the sensory quality was unacceptable at 200 d. The sensory quality of Antarctic krill frozen at -30 °C was acceptable at 200 d. The quality of Antarctic krill frozen at -40 °C and -50 °C was better. At 200 d, the sensory quality was acceptable, and the quality of Antarctic krill frozen at -40 °C and -50 °C was better.	Li et al. (2014)
-20, -40, -80 °C	<i>Eriocheir sinensis</i>	lipid oxidation indexes at -20 °C was higher than at -40 and -80 °C, and the degree of lipid oxidation was the least at -80 °C. At the same frozen time, POV, AV and AnV at -80 °C increased the lowest compared with those at -20 °C and -40 °C, and the frozen storage slowed down the occurrence of the lipid oxidation reaction.	Fan et al. (2022)
-18, -28, -60 °C	Squid	Sensory evaluation, pH and salt-soluble protein content decreased; TVB-N, TBA value and K value increased and squid quality ranked: -18 °C < -28 °C < -60 °C.	Gao (2019)

issue structure (Mulot et al., 2019). At the molecular level, the α -helix structure of myofibrillar proteins molecules changed and transformed into β -sheet and random coil, resulting in a greater reduction in the tightness and stability of protein conformation (Qian et al., 2022b). The enzyme activity decreases and the textural properties are better maintained in freezing temperature, which protects the quality of aquatic products better. Therefore, a lower freezing temperature than the conventional freezing temperature ($-18\text{ }^{\circ}\text{C}$) should be used as much as possible, taking into account the economics.

2.2 Freezing methods

Common freezing methods for aquatic products include air freezing, blast freezing, and dip freezing. The ice crystals, produced during the freezing process, could cause mechanical damage to the muscle, leading to a series of chemical reactions, such as lipids oxidation, and protein freezing denaturation (Song et al., 2017). Liquid nitrogen quick-freezing of fresh balsa fish took the shortest time, caused the least mechanical damage to the product, the freshness and quality were guaranteed (Hu et al., 2021). On this basis, by comparing the effects of liquid nitrogen immersion time, interval time and number of immersions on quick-frozen fish balls, and a batch of fish ball products were obtained that were superior to traditional production methods in terms of color and texture, which also provided some theoretical basis for modernized quick-frozen industrial production (Lei et al., 2020). Previous study found that immersion freezing and liquid nitrogen freezing preserved the water-holding capacity of grass carp muscles, and observed smaller, more regular intracellular ice crystals, compared to air freezing (Diao et al., 2021). Therefore, it is more effective to use immersion freezing and liquid nitrogen freezing to improve the quality of frozen fish if technically and economically allowable.

2.3 Freezing rate

Rapid freezing is usually defined as the food passing through the central temperature of the maximum ice crystal formation zone ($-1\text{ }^{\circ}\text{C}$ to $-5\text{ }^{\circ}\text{C}$) within 30 minutes. Conversely, it is called slow freezing if the food passes through the maximum ice crystal formation zone in more than 30 minutes. Slow freezing rates lead to an increase in the number of ice crystals, which can cause the nucleus to form large extracellular ice crystals and disrupt the structure of muscle tissue (Cai et al., 2018).

The relationship between freezing rate and ice crystal shape is presented in Table 2. The size, location and distribution of ice crystals are related to freezing speed. During the rapid freezing process, small and numerous ice crystals are generated within the cells, while the slow freezing process generated larger and

aggregated intercellular ice crystals. Ultrasound-assisted freezing, compared with cold air freezing, could significantly increase the freezing speed and better maintain the quality of frozen large yellow croaker. The quality parameters of the samples after triple ultrasonic-assisted freezing treatment were closer to those of fresh samples, and the formed ice crystals were fine and uniformly distributed, and the tissue damage was less (Ma et al., 2021). By comparing the effects of ultrasonic-assisted freezing and low-temperature quick-freezing on the morphology of perch ice crystals, it was found that the fish fillet samples treated with ultrasonic-assisted freezing at $-40\text{ }^{\circ}\text{C}$ had a faster freezing rate and a small and uniform distribution of ice crystals (Li et al., 2021).

3 The impact of frozen aquatic product quality in frozen storage

Quality generally includes sensory quality and physiochemical quality. Sensory quality is mainly evaluated by indicators such as appearance, color, odor and taste, which can influence consumer preferences. Physiochemical quality mainly refers to the nutritional quality and safety quality of the product (Mu et al., 2019).

3.1 Sensory quality changes

Sensory evaluation is the use of touch, taste, smell, etc. to perceive the characteristics of the evaluation object. Sensory evaluators can quickly judge the quality changes of aquatic products by scoring the sensory evaluation indicators such as appearance, odor, taste, and texture (Jiang et al., 2021b). The more obvious sensory changes in frozen aquatic products are their color, texture and flavor. For example, the phenomenon of blackening of the head of *Euphausia superba* during the freezing process, the yellow color of the fish body of *Larimichthys crocea* faded with the prolongation of storage time, and there was no significant change in first 10 d of frozen, and when it reached 90 d, the muscle showed flabby, elastic and poor taste. The consumer acceptance of the product quality decreased significantly. At the same time, due to the long freezing storage period, the frozen and then boiled *Euphausia superba* showed strong irritating flavor such as fishy taste and ammonia, which were obviously unacceptable to the senses (Li & Sang, 2015; Li et al., 2014). Five professional sensory evaluators were selected to evaluate the sensory of squid at $-18\text{ }^{\circ}\text{C}$, $-28\text{ }^{\circ}\text{C}$ and $-60\text{ }^{\circ}\text{C}$, combining TVB-N values, thiobarbituric acid values and salt-soluble protein content, and the results showed that the lower freezing temperature was more effective in delaying the decline of sensory quality of squid (Gao, 2019).

The sensory evaluation method is quick and easy, and a professionally trained sensory evaluation team can assess all these sensory characteristics well. Otherwise, the evaluation score is

Table 2. Relationship between freezing rate and ice crystal shape (Cai et al., 2018).

Freezing time	Crystallization position	Ice crystal shape	Ice crystal size (diameter x length)
Several seconds	Intracellular	Needle-shaped	(1~5) μm \times (5~10) μm
1.5 min	Intracellular	Rod-shaped	(0~20) μm \times (20~50) μm
40.0 min	Intracellular	Columnar	(50~100) μm \times 100 μm
90.0 min	Extracellular	Block granular	(50~200) μm \times 200 μm

easily affected by the physical and psychological condition of the assessor, and has certain limitations, so to accurately determine the impact of freezing on the quality of aquatic products usually also need to use electronic technology, such as E-tongue, E-nose and other instruments to detect the taste and odor of aquatic products, and physicochemical quality combined with the sensory evaluation results for calibration (Lopes et al., 2022).

3.2 Changes in physicochemical properties

Microstructural structure

The size, shape and location of ice crystals and the degree of damage to muscle tissue can be observed by analyzing the microstructure. Organizational structure is an important indicator for evaluating the quality of frozen aquatic products. There are two ways to observe ice crystal morphology, direct and indirect. Ice crystals were observed directly by cryo-optical microscopy and infrared spectroscopy, while the gaps between ice crystals and tissue were observed indirectly by cryosectioning (Cai et al., 2018). The structure of ice crystals formed during freezing was analyzed indirectly through four parameters: cross-sectional area, equivalent diameter, roundness, and stretch. The electron micrographs of the changes in the aquatic product structure under different treatments are shown in Figure 1.

Frozen tuna after light marinade had reduced or disappeared interstitial spaces and improved fish quality characteristics (Jiang et al., 2021a). Ice crystals formed in the intercellular space of frozen crispy fish muscle compared with muscle fibers from fresh samples, causing aggregation of tissue muscle fibers and resulting in decreased water retention (Chen et al., 2019b). The cinnamaldehyde/starch/PVA membrane, using to wrap large yellow croaker, effectively inhibited the oxidative folding of proteins, resulting in tighter binding of muscle tissue. Compared with commercial antifreeze (sodium pyrophosphate and arabinoside), the myofibril orientation of scallop adductor muscle treated with protein peptide (derived from wheat) was

still clearly visible, and the myofibril bundles were tightly packed with minimal breakage (Shi et al., 2022).

Water holding capacity

The water content in the muscle of freshwater fish is relatively high, generally accounting for 75-80% of the fish body weight. It is mainly present in the space inside and outside the muscle fibers. Therefore, key changes in intracellular structure affect the ability of muscle cells to retain water (Yu et al., 2018; Leygonie et al., 2012). Many factors could affect water holding capacity, such as protein denaturation and ice crystal recrystallization (Figure 2). By monitoring the thawing loss and centrifugal loss of frozen preserved grass carp for 24 weeks, it was found that myofibrillar proteins denature and aggregate with increasing frozen storage time, leading to a decrease in water holding capacity within frozen grass carp muscle, regardless of the freezing method used (Diao et al., 2021). It was found that centrifugal losses of frozen bighead carp fillets increased from 7.67% to 13.17% in the control group and from 13.17% to 26.50% after 9 months of frozen storage. The results of centrifugal and cooking losses indicated that the decrease in water holding capacity of bighead carp fillets was attributed to the compression of muscle fibers by ice crystals and recrystallization, which caused deformation of myogenic fibers and oxidation of myogenic fibrillar proteins (Liu et al., 2022).

pH value

The accumulation of metabolites from biochemical reactions and enzymatic catabolism can cause pH changes, and to some extent reflects the freshness of the sample to be tested. Since pH has a direct effect on the stability of proteins, it has a great influence on the water holding capacity of aquatic products. When the pH reaches the isoelectric point of the main proteins in aquatic products, the polar groups of the proteins would attract each other, thus reducing the water-holding capacity. In general, pH varies greatly depending on the type of food, the processing

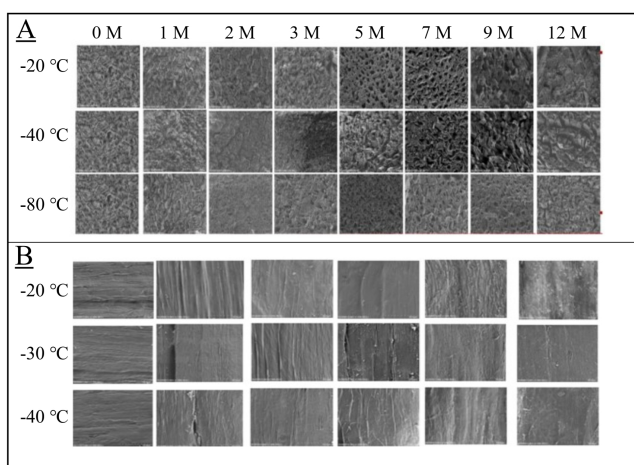


Figure 1. Changes in the microstructural structure of different frozen aquatic products under different treatment methods. (A): Frozen Tilapia Fillets, (B): *Eriocheir sinensis*.

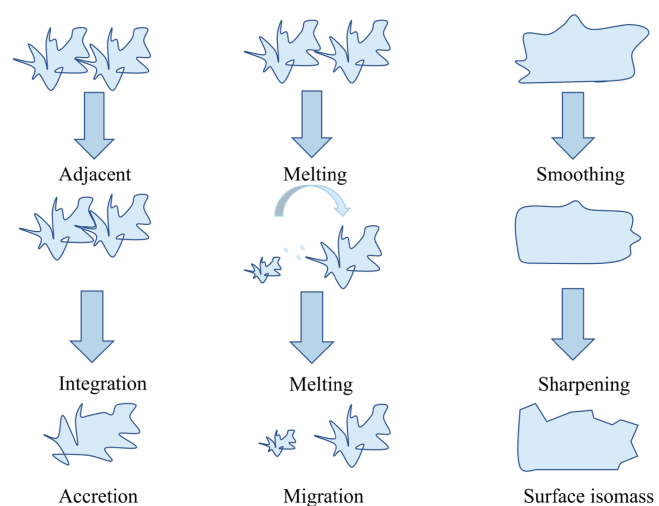


Figure 2. Three mechanisms of recrystallization (accumulation, migration and surface isomass).

method and the type of microorganisms contaminating it, so pH is mainly used as an indicator of late spoilage. Through the study of catfish treated with NaHCO_3 , it was found that the decrease in pH of catfish meat after immersion occurred due to the accumulation of acidic substances such as lactic acid and fatty acids due to the influence of glycolysis, free amino acids and amines produced by denaturing degradation of proteins (Zhang et al., 2020). The pH value of squid under different refrigeration temperatures showed an overall trend of first decreasing and then increasing in the range of 6.2-7.0, and the presumed reason was due to the lactic acid and phosphoric acid produced by glycogen and adenosine triphosphate in the muscle, which led to a decrease in pH at the beginning of storage; with the extension of storage time, the muscle itself underwent digestion and protein decomposition, producing amino acids and other nitrogenous compounds, and the pH value showed an increase. As the storage time increases, the muscle itself undergoes digestion and protein decomposition, producing amino acids and other nitrogenous compounds, and the pH shows an increasing trend (Gao, 2019).

3.3 Protein oxidation

Fish, shrimp, shellfish and crabs are protein-rich and protein denaturation usually occurs during frozen storage and causes a decrease in the nutritional and functional quality of aquatic products. Side chain modification of amino acid residues is a major change resulting from protein oxidation, and almost all amino acid side chains can be modified by oxidation (Jiang et al., 2016). The oxidative modification of side chain amino acids is specified in Figure 3, where oxidative stresses such as reactive oxygen species attack the backbone proteins through which will in turn lead to changes in the secondary and tertiary structure and conformation of the protein.

The most commonly used measurement methods include differential scanning calorimetry (DSC) and sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE). In addition, to reflect the changes in protein structure during the freezing

period, common indicators such as total sulfhydryl content, carbonyl groups, free amino groups, and Ca^{2+} -ATPase activity are usually used. And in recent years spectroscopic methods, such as Fourier transform infrared spectroscopy, circular dichroism, characteristic fluorescence emission spectroscopy, and Raman spectroscopy have also been frequently used to detect changes in protein structure (Nian et al., 2019).

In a protein characterization study of open-back seasoned fish by (Wu et al., 2021), it was found that the oxidation of fillet proteins increased with the increase in the number of freeze-thaws, as evidenced by a decrease in the total sulfhydryl content and an increase in the content of disulfide bonds formed by the oxidation of sulfhydryl groups. The indicators of salt-soluble protein content, surface hydrophobicity, carbonyl group and active sulfhydryl group content were used in *Haliotis Discus Hannai Ino* columns, the carbonyl group content decreased significantly while the active sulfhydryl group content increased significantly, similar to the above results, i.e., the freeze-thaw cycle during freezing accelerates the oxidative denaturation of proteins, causing nutritional loss and physicochemical changes of aquatic products. The freezing cycle will accelerate the oxidative denaturation of proteins, causing nutritional loss and physicochemical changes in aquatic products, thus affecting the physicochemical and sensory quality of aquatic products (Yin, 2020).

3.4 Lipid oxidation

Although subzero cold temperatures can inhibit almost all reactions in the organism, some biochemical reactions can still occur, including lipid oxidation and lipid hydrolysis. Most existing studies have focused on physical changes and protein denaturation. However, few studies have addressed lipid oxidation and hydrolysis. Fish and other aquatic products are widely used in experimental studies because of large amounts of polyunsaturated fatty acids that are easily oxidized to lower fatty acids, aldehydes, and ketones (Araújo et al., 2022; Yin et al., 2022), lipid oxidation product-protein interactions that lead to changes in the functional structure of proteins, resulting in deterioration of flavor, color, and texture.

Ice crystals can damage cells and induce the release of oxidants that can accelerate lipid oxidation, while lipid oxidation products are also prone to react with proteins, leading to alterations in their sensory and quality (Wang et al., 2018). These deteriorations are caused by toxic compounds such as malondialdehyde (MDA) and cholesterol oxidation products caused by oxygen radicals or lipid radicals. 2-Thiobarbituric acid value (TBARS) can be generated by the reaction between thiobarbituric acid (TBA) and malondialdehyde (MDA) and is used to reflect the amount of fat oxidation secondary products and is an important indicator of fat oxidation (Figure 4). In catfish that underwent repeated freeze-thaw cycles (Zhang et al., 2020), damage to muscle tissue structure by ice crystals increased the contact area of lipids with air, resulting in a significant increase in acid value, TBA values, a significant deterioration in odor, a significant increase in whiteness values and causing a significant loss of juice.

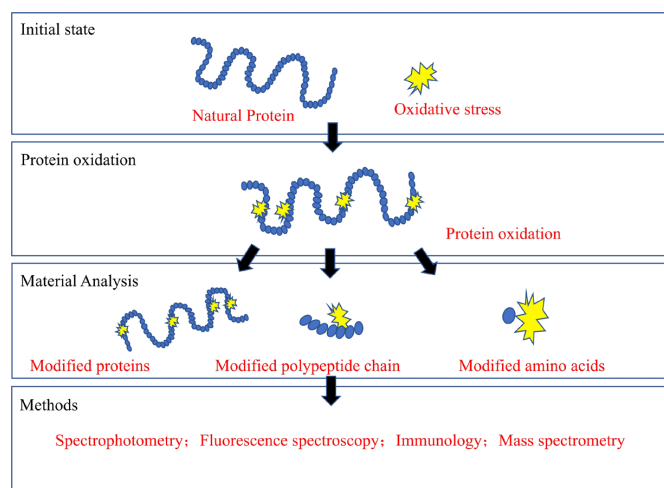


Figure 3. Schematic diagram of protein oxidative modification analysis (Kehm et al., 2021).

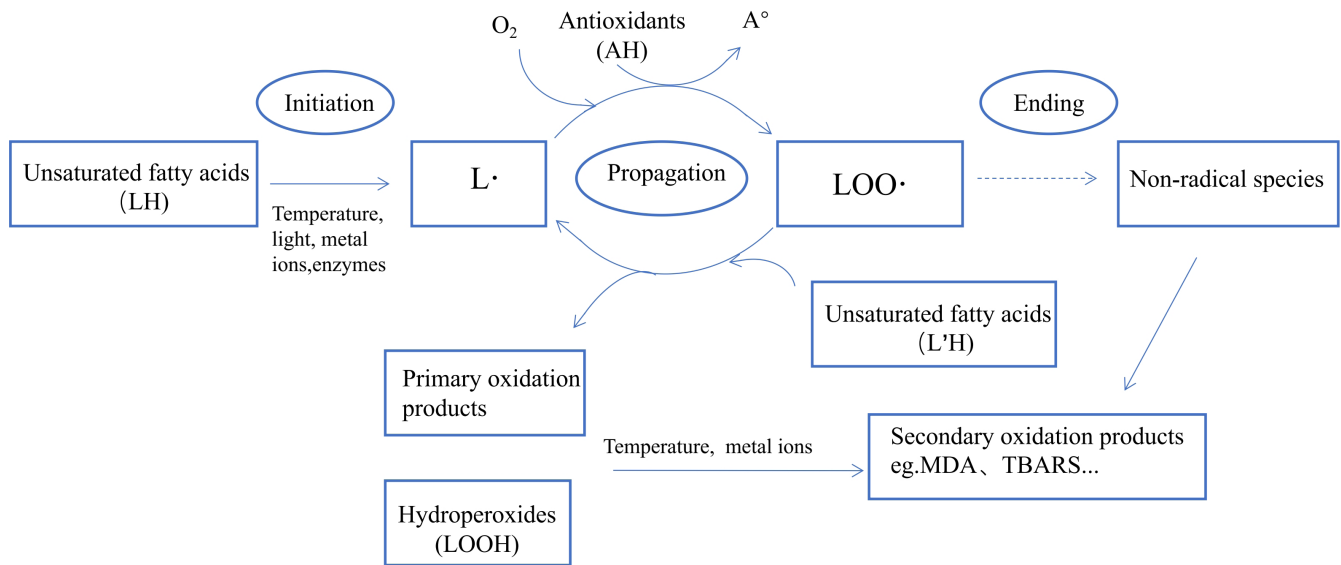


Figure 4. Lipid oxidation mechanism diagram (Guyon et al., 2016).

4 New technology to improve the quality of frozen aquatic products

Frozen aquatic products after low-temperature storage, due to fat oxidation and protein oxidation and other deterioration phenomena, resulting in the decline of the economic value of aquatic products. In order to alleviate the problem of ice crystal recrystallization, so to take some measures to intervene, mainly from the new freezing technology, adding natural green antifreeze and new active packaging technology to control the quality of frozen aquatic products in three aspects. For example, new quick-freezing technology means are used to assist in freezing foods, such as high-pressure freezing (Zhan et al., 2018), ultrasound-assisted dipping freezing (Sun et al., 2019), and electromagnetic wave-assisted freezing (Hafezparast-Moadab et al., 2018). the quality of aquatic products is improved by adding substances such as natural antifreeze agents, polysaccharides, and plant essential oils to aquatic products, such as antifreeze proteins (Shi et al., 2022), plant polysaccharides, marine polysaccharides, and plant essential oils, new food packaging technologies are used, and active films are with antibacterial, antioxidant and other active substances with specific functions, such as polysaccharide coated films, protein coated films and some composite films (Mohamed et al., 2020).

4.1 Application of new freezing techniques

Traditional freezing techniques, such as air freezing and dip freezing, can produce large and irregular ice crystals thus leading to muscle damage and nutrient loss. Therefore, new freezing techniques have also been developed in recent years. For example, (1) high-pressure assisted freezing method can effectively promote the formation of small ice crystals during freezing, which can be divided into three types: pressure transfer freezing method, pressure assisted freezing method, and pressure induced freezing. It was found that the frozen stored tuna at 200 MPa

high-pressure treatments had better acceptability and a reduction in the total number of bacteria, which prolonged the shelf life of the samples, but during the pressurization process, the state of the samples should be taken into account, and too high pressure can lead to changes in muscle appearance (Kamalakanth et al., 2011). (2) Electromagnetic wave-assisted freezing techniques based on electromagnetic fields include electric field-assisted freezing, magnetic field-assisted freezing, radiofrequency-assisted freezing, and microwave-assisted freezing, among which microwave-assisted and radiofrequency-assisted freezing are commonly used for aquatic products freezing. (Manzocco et al., 2022) optimized the previously proposed RF-assisted nitrogen cryogenic freezing by setting up continuous cryogenic freezing (ccf) lasting 2.5 min and pulsed cryogenic freezing (pcf) with 3 s pulses at 10 s intervals lasting 10 min. The conventional slow freezing and blast freezing samples were used as controls, and when frozen under RF-assisted continuous cryogenic freezing, the hardness did not differ much from that of fresh samples, and drip loss was only 1%, indicating that RF is effective as an adjunct technique to prevent cell damage caused by nitrogen flow alone, and changing the nitrogen delivery from continuous to pulsed mode appears to be more effective in preventing hardness changes. Pulsed cryogenic freezing actually exhibited hardness comparable to fresh samples and resulted in additional drip loss reduction (< 1%), accounting for the lowest mean value. RF-assisted freezing improved the hardness of the samples and reduced exudate loss during thawing. RF application was particularly effective in maintaining tissue microstructure, possibly by limiting myogenic fiber denaturation, thereby facilitating the retention of fixation water within the cells. (3) Ultrasonic-assisted dip freezing is a novel and promising freezing technique in the food industry. During the freezing process, the propagation of ultrasonic waves in the medium produces various physical and chemical effects, such as cavitation effects, breakage of ice crystals, and release of reactive groups, which can be used to improve the quality of frozen foods (Tian et al., 2020). Among

these effects, cavitation is the most important phenomenon, since cavitation can produce bubbles. The rupture of bubbles can induce ice nucleation, accelerate heat transfer, and promote the fragmentation of large ice crystals into finer and more uniform ice crystals. Depending on the frequency and intensity of the application, ultrasound can be divided into high-frequency and low-intensity ultrasound (> 100 kHz), and low-frequency and high-intensity ultrasound or power ultrasound (between 20 and 100 kHz), the latter being often used in food processing (Awad et al., 2012). However, for UIF, it is recommended to use both low-frequency and low-intensity ultrasound, which both shortens the freezing time and has improved water holding capacity and textural properties of aquatic products.

4.2 Adding natural green anti-freeze agent

The addition of antifreeze is one of the effective methods to alleviate the quality deterioration of frozen foods in the cold chain process, and most of the commercial antifreezes in food are polyphosphates, sugars, alcohols and their complexes, but there will be some restrictions for some special populations, such as diabetic patients, hypertension and kidney disease patients (Shen et al., 2019), while some studies found that organisms produce antifreeze proteins in cold environments, which are proteins that control the growth of ice crystals and recrystallization of ice-structured proteins that function as a defense against cold temperatures. Antifreeze proteins are widely present in different cold-tolerant species and can be observed in various organisms such as microorganisms, fish, insects, plants, and vertebrates. Antifreeze proteins have the ability to inhibit ice crystal growth, hinder recrystallization caused by freeze-thaw cycles, alter ice crystal morphology and protect cell membranes (Baskaran et al., 2021). The currently accepted

mechanism of action of antifreeze proteins is the adsorption-inhibition mechanism, which suggests that antifreeze proteins irreversibly adsorb to specific surfaces of ice crystals and inhibit their growth. This can be seen in Figure 5.

The interaction between herring antifreeze protein and ice crystals was studied by molecular dynamics simulation. On this basis, the effect of herring antifreeze protein on the quality attributes of largemouth bass after three freeze-thaw cycles was investigated. The results showed that immersion of fish samples in herring antifreeze protein solution prior to freezing and storage helped to reduce damage to fibrous structures and minimize drip loss from thawed samples (Nian et al., 2020). To address the deterioration of frozen surimi quality during the freeze-thaw cycle, Antifreeze protein was added to surimi to prevent the denaturation of surimi proteins by reducing the loss of Ca²⁺-ATPase activity, slowing the oxidation of sulfhydryl groups to disulfide bonds, maintaining the surface hydrophobicity and protein solubility of surimi proteins, and weakening the effect of frozen storage on the mobility of bound water (Chen et al., 2022). In contrast, by adding antifreeze proteins and vacuum impregnating the closed-shell muscle of scallops, it was confirmed that antifreeze proteins can adsorb the surface of ice crystals thus inhibiting the growth of ice crystals and modifying the morphology of ice crystals, which can effectively regulate the quality of frozen products.

4.3 Application of active packaging technologies

Many emerging technologies for frozen storage of aquatic products have been developed, such as ice coating (Wu et al., 2022), vacuum packaging, and active (antibacterial/antioxidant) coating (Zong et al., 2020), which have been shown to be

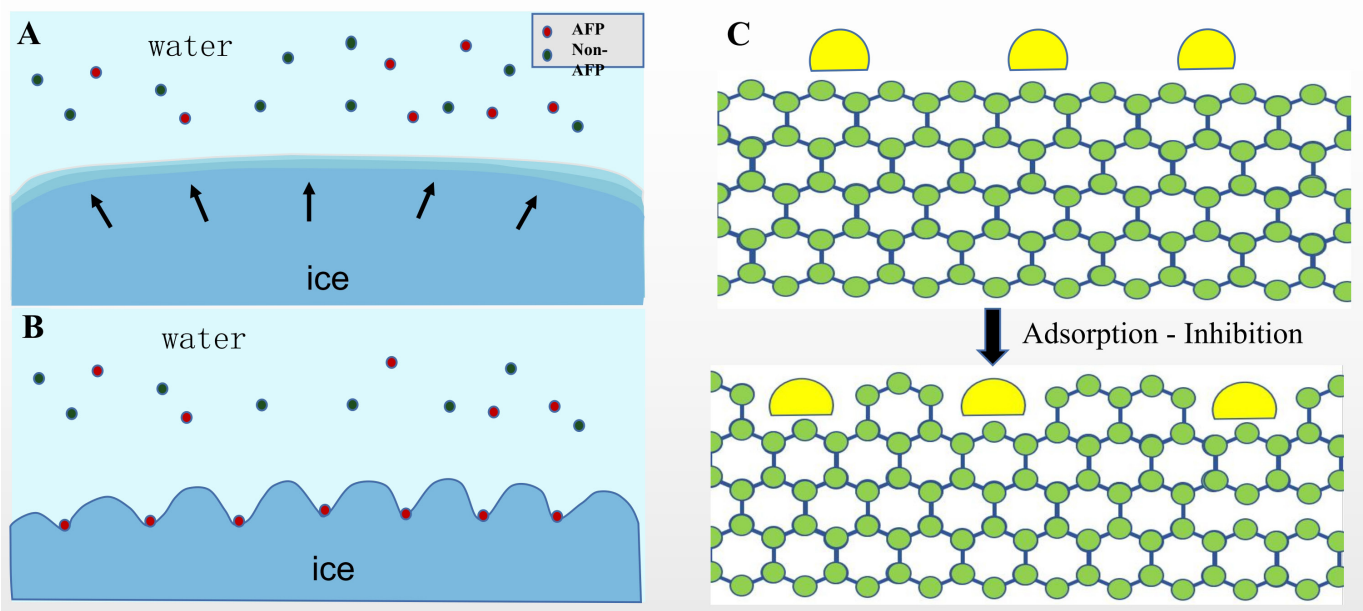


Figure 5. Schematic figure of antifreeze protein (AFP) ice inhibition via the Gibbs-Thomson effect. (A) A mixture of AFP and non-AFP proteins ahead of a growing ice front. (B) AFPs selectively bind to the ice, while non-AFPs are excluded. (C) Schematic diagram of adsorption-inhibition mechanism. Note: The yellow hemisphere represents antifreeze protein, the cyan spheroid represents ice crystals, and free water molecules are not shown (Kuiper et al., 2015).

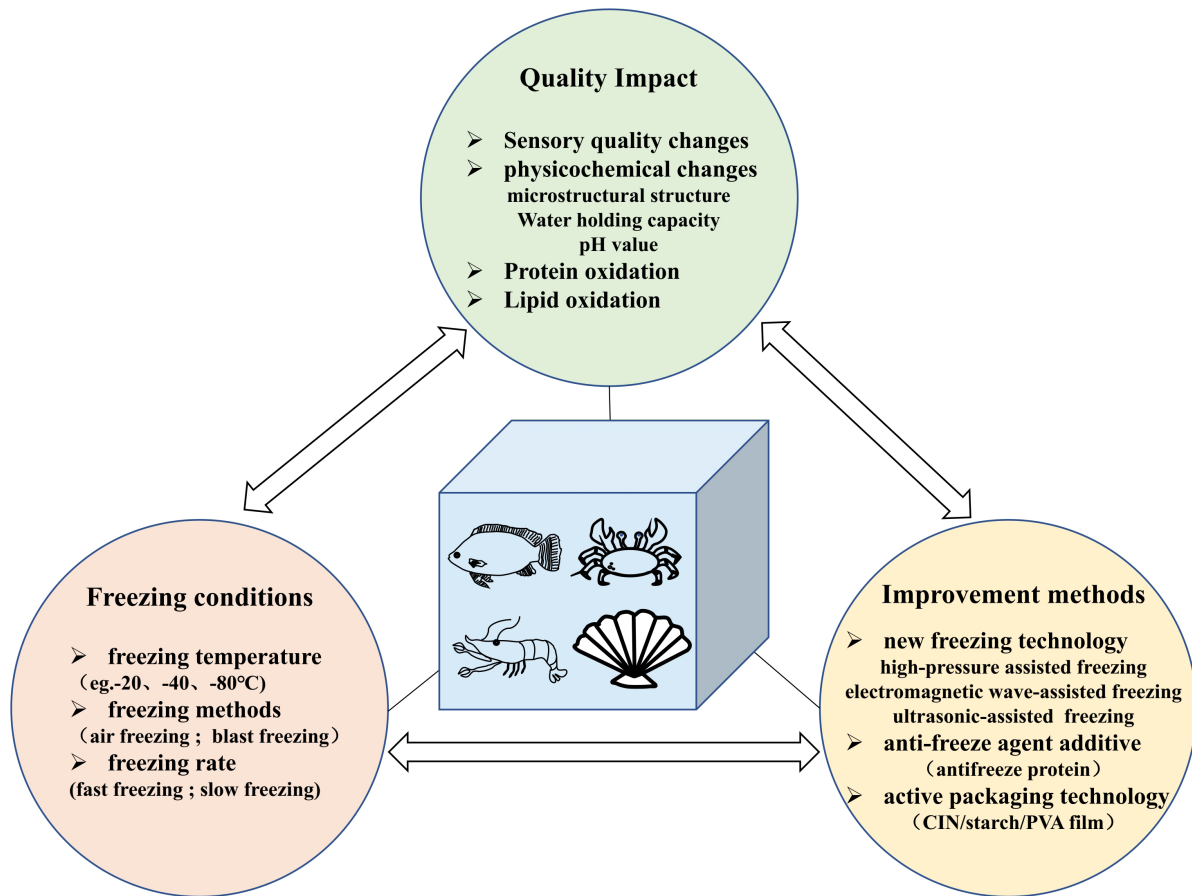


Figure 6. Changes in the quality of frozen aquatic products and improvement measures.

beneficial in extending the shelf life of frozen aquatic products (Lira et al., 2021). However, the ice coat or coating combined with the aquatic product exhibits the disadvantages of affecting the sensory attributes of the product and increasing the weight of the product, leading to a certain degree of reduction in the consumer experience. In contrast, active packaging films can avoid these disadvantages, while adding active substances to the films can make the prepared films with antibacterial and antioxidant functions, which have the advantages of simple operation, low equipment requirements, and significant effects, which can delay their spoilage and deterioration and extend the shelf life of food products (Chen et al., 2020).

Starch/PVA films inhibited water loss, water migration, protein degradation, lipid oxidation, and microstructural damage in *Pseudosciaena crocea*. The films containing CIN treated with higher moisture content provided the best protection to *Pseudosciaena crocea* (Zong et al., 2022). In addition, it was found that the sensory quality, lipid peroxide value, total bacterial colony count, volatile salt nitrogen and pH of the group treated with polyvinyl alcohol/nano-titanium dioxide/anthocyanin films were better than those of the blank and pure polyvinyl alcohol films. The total number of colonies reached 7.111 cfu/g at the 16th day of storage, while the other experimental groups reached 7.141 and 7.031 cfu/g at the 12th day of storage, and their shelf life was extended by 4 d (Tang et al., 2019).

5 Conclusion

In order to better extend the cycle of aquatic products circulation in the market, freezing is still a generally effective and worthy of research preservation means. From the analysis of the factors that have a more serious impact on the quality of aquatic products, the main common indicators (sensory evaluation, physical indicators, chemical indicators) that can reflect the changes in the quality of aquatic products during freezing are selected to avoid the subjectivity and one-sidedness brought by a single evaluation index. Current methods on improving the quality of aquatic products are mainly focused on new freezing technologies, natural anti-freeze agents and active packaging technologies (Figure 6).

Although the problem of quality deterioration of frozen aquatic products can be greatly overcome, the mechanisms for new auxiliary freezing technologies, such as ultrasonic-assisted freezing and electromagnetic-assisted freezing, are still not fully understood, and further comprehensive models of quality are still needed to elaborate the mechanistic changes in the freezing process. In addition, although the novel technologies are effective in improving the quality of aquatic products, most of the existing research results are limited to laboratory conditions, and better application of experimental results to industry has been a challenge. Therefore, future research can focus on translating the laboratory results into industrial applications and on the

continuous optimization of novel technologies to improve the shelf life of aquatic products and to maximize the utilization of aquatic resources.

Conflict of interest

The authors declare no conflict of interest.

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