Lecture-7 Food Preservation by Freezing

Course Code: NFE-111
Course Title: Introduction to Food Science and Technology
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Freezing in Biological Materials

Freezing provides a significant extended shelf life and has been successfully employed for long-term preservation of many foods. Freezing is still one of the most widely used methods of food preservation even though several new technologies, such as high pressure, infrared irradiation, pulsed electric field, and ultrasound, are gaining importance. Freezing processes are continuing to emerge. Freezing changes the physical state of a substance by changing water into ice when energy is removed in the form of cooling below freezing temperature. Usually, the temperature is further reduced to storage level (e.g., —18°C). The freezing process can be clearly shown by using freezing or cooling curves and phase diagrams. The terminologies of the freezing process (e.g., precooling, supercooling, freezing, tempering, eutectic, ice nucleation, and glass transition) are discussed in Chapter 15.

Mode of Preserving Action

The freezing of foods slows down, but does not stop, the physicochemical and biochemical reactions that govern the deterioration of foods [69]. During storage, there is a slow progressive change in organoleptic quality, which does not become objectionable for some time [176]. The loss of quality of frozen foods depends primarily on storage temperature, length of storage time, and thawing procedure. Microbial growth is completely stopped below –18°C, and both enzymatic and nonenzymatic changes continue at much slower rates during frozen storage [142].

The freezing process reduces the random motion and rearrangement of molecules in the matrix [88,111,142]. Freezing involves the use of low temperatures, and reactions take place at slower rates as temperature is reduced. The presence of ice and an increase in solute concentration can have significant effects on the reactions and the state of the matrix [167]. The final influence of temperature on chemical reactions due to freezing could be grouped as: (a) normal stability (a temperature decrease results in a slower reaction rate, thus better stability when foods are stored); (b) neutral stability (the tempera- ture has no influence on the reaction rate); or (c) reversed stability (a temperature decrease results in an increased reaction rate) [159]. Regardless of the type of aqueous system, concentration during freezing causes the unfrozen portion to undergo marked changes in physicochemical properties such as ionic strength, pH, viscosity, water activity, surface and interfacial tension, and oxidation–reduction potential. It is important to note that oxygen is almost totally expelled from ice crystals as they are formed [159]. Reid [167] reviewed three types of cell damage due to freezing: osmotic damage, solute-induced damage, and structural damage.

In slow cooling, ice forms slowly in the external cells. If there is sufficient time, water from the cells migrates out by osmotic pressure. This results in cell shrinkage and some membrane damage. This water does not return to the cells on thawing due to the damage to the cell wall, and the consequence is drip loss [167]. The concentration of the solute increases as freezing progresses. Thus, high solute concentrations of the unfrozen matrix, in particular high salt, can cause damage to many polymeric cell components and may kill the cell [139]. This concentration effect is present irrespective of whether freezing is fast or slow. Cryoprotectants, such as sugars, are usually added to the aqueous phase to reduce salt-induced damage [167]. In addition to the concentration effect, the formation of ice within the cell may cause damage to the delicate organelle and membrane structure of the cell. As a consequence, enzyme systems may be released, leading to a variety of effects, including off-flavor production. This can be prevented by blanching, a prefreezing heat treatment that denatures enzymes [167].

Quality of Frozen Foods

Freezing Rate and Quality

Controlling the freezing process, including careful prefreezing preparation and postfreezing storage of the product, is an important aspect of achieving a high-quality product [69]. An important factor in the quality of frozen foods is the freezing rate [186]. Generally, fast freezing produces better quality frozen food than slow freezing, although the reason for this is not as well understood as is sometimes stated. The rate of freezing of plant tissue is important because it determines the size of the ice crystals, cell dehydration, and damage to the cell walls. Ice crystal structure is crucial for the preservation of the quality of frozen products [211].

In the case of animal tissue, the concentration of salt within the cells is higher than that in the extracellular region. Consequently, freezing will start outside the cells due to the freezing point depression induced by the solute concentration in the cells. As soon as ice appears, the solute concentration rises. This is a characteristic phenomenon of freeze concentration. At some point, osmotic pressure difference causes water to flow through the semipermeable cells to the extracellular region to balance the chemical potentials. This dehydration of the cell is accompanied by shrinkage of the cell, which is not normally lethal. The freezing rate affects this process because rapid freezing results in less cell dehydration (since water has less time to diffuse out of the cell), less breakage of cell walls, and less textural damage. The more rapid the crystallization, the smaller the ice crystals, and the lesser the damage caused by the process of freeze concentration. Consequently, a reverse situation holds for thawing. Slow heating allows equilibrium to be reached as the melted water diffuses back through the cell wall.

In the case of plant tissue, there is evidence that large ice crystals can cause mechanical damage to cell walls in addition to cell dehydration. In agarose gels, large ice crystals (100–300 μm) with increasing interstitial spaces grow under slow freezing conditions at –25°C, while small ice crystals (1–2 μm) form during rapid freezing in liquid nitrogen [12]. Bevilacqua et al. [16] measured the diameter of the intracellular dendrites and extracellular ice crystals for meat frozen under simulated conditions similar to industrial freezing. They correlate the ice crystal diameter with the characteristic freezing time. De Kock et al. [40] studied the effect of freezing rate (cryogenic, fast; mechanical, slow) on the quality of cellular and noncellular precooked starchy foods. Quality was determined immediately after freezing, as well as after frozen storage, by chemical, physical, microscopic, and sensory methods. The rapid freezing of cellular starchy food resulted in a better quality product than slow freezing immediately after freezing. Rapid freezing of noncellular starchy food, however, produced a product that was only slightly better in quality than the slowly frozen product. After storage, the rapidly frozen cellular product was still better in quality than the slowly frozen product, although the difference was smaller. The slight advantage gained by rapid freezing of the noncellular product was lost during storage [40].

Symons [187] expressed that undue emphasis on the importance of freezing speed is sometimes misleading. Unless freezing is excessively slow, days or weeks rather than hours, most products are comparatively insensitive to the speed of freezing. In any case, an increase in volume of around 10% is associated with freezing of most foods. Broadly speaking, faster is marginally better than slower in most of the food products. This is particularly true for fruit and vegetable products, but less so for animal tissue [187]. Moreover, the initial advantage obtained by fast freezing is lost during storage due to recrystallization [40]. Although fast freezing has advantages, some products will crack or even shatter if exposed directly to extremely low temperature for a long period of time. Hung and Kim [88] reviewed the fundamental aspects of freeze cracking and strategies for its prevention. The mechanisms to explain freeze cracking vary. The proposed mechanisms are

1. *Volume expansion*: The volume expansion due to the formation of ice and the amount of empty space in a microstructure are the primary factors affecting the degree of mechanical damage to cells during freezing. In addition, differences in moisture content, composition, or amount of unfreezable water may cause different degrees of cracks [55].
2. *Contraction and expansion*: Cracking may also occur to relieve the product of internal stress from nonuniform contraction during rapid cooling [165,209]. However, both contraction and expansion may cause freeze cracking [175].

3. *Internal stress*: Fast freezing will cause crust formation at the surface, which serves as a shell and prevents further volume expansion when the internal portion of the unfrozen material undergoes freezing. This process then contributes to the internal stress buildup later in the freezing process. The freeze cracking will occur if the internal stress exceeds the strength of the exterior frozen material during processing [105]. The distribution of the stress is the controlling factor, and it is governed by absorbing (dissipating) the stress into the structure or reflecting the stress to cause buildup of internal stress [106].

Miles and Morley [140] studied the internal pressures and tensions in meat during freezing, frozen storage, and thawing. A maximum stress of almost 6000 kPa is possible. They found that during freezing internal compression developed at a rate that increased as freezing progressed, and most of the pressure was developed after the center had started to freeze. Generally, the circumferential tension in the outer surface of the muscle reached a breaking point, and a shallow crack formed along the length of the muscle or the surface yielded, causing a bulge [140]. Kim and Hung [106] found that size, moisture content, density, modulus of elasticity, Poisson's ratio, and porosity all had significant influence on freeze cracking. However, no single property completely explained the development of freeze cracking [106]. Excessive freezing speeds can ruin a food product. The buildup of internal pressure during very rapid freezing shatters the already frozen external layers and produces very small crystals, leading to scattering of incident light [187]. The current practice of quick freezing is generally chosen to save processing time (cost) and factory space. Moreover, rapidly chilled muscles become tough on freezing and thawing, a phenomenon known as cold shortening, which is not a problem in poultry [187].

In foods containing microbial cultures, it is important to maintain their activity. Rapid freezing causes detrimental effects on yeast activity of frozen dough. This may be due to the formation of intracellular ice crystals invariably lethal to yeast cell membranes [138]. Yeast activity decreased significantly when the rate of cooling was increased from 0.98 to 1.57°C/min [146].

26.1.2 Microbial Aspects

The detrimental effects of freezing on microorganisms may be desirable or undesirable, depending on the types of food products. In frozen foods without any added beneficial cultures, microbial growth or spoilage is not desirable, whereas care must be taken to reduce the damage in cells during freezing of foods containing microbial cultures. The maximum recommended storage temperature at which microbiological spoilage ceases is registered between —9°C and —12°C. Although microbiological spoilage can be avoided at these temperatures, the enzymes present in the product will still play a part in spoilage. Hence, hygienic conditions or heat processing (blanched or cooked) will increase the shelf life [187]. Freezing causes the apparent death of 10%–60% of the viable microbe population, a percentage that gradually increases during frozen storage [142]. Microorganisms differ considerably in their sensitivity to freezing; thus, the main concern is organisms that are likely to survive the freezing treatment and grow when the product is thawed. There is considerable variation in the ability of bacteria to resist damage by freezing [4]. In general, Gram-negative bacteria are less resistant to freezing death than are Gram-positive bacteria. Nonsporulating rods and spherical bacteria are the most resistant, while bacterial spores, such as *Clostridium* and *Bacillus*, remain unaffected by freezing. Bacteria in the stationary phase are more resistant than those in the log phase [4,142,154,176]. Genera commonly encountered in frozen food include *Pseudomonas*, *Achromobacter*, *Flavobacter*, *Micrococcus*, *Lactobacillus*, *Corynebacterium*-like catalase-positive rods, enterococci, *Streptococcus lactis*, *S. lactis*-like streptococci, *Aerococcus*, and *Pediococcus* [142,184]. Gianfranceschi and Aureli [70] studied the survival of *Listeria monocytogenes* during freezing (—50°C) and frozen storage (—18°C) when inoculated into chicken breast, ground beef, spinach, mozzarella cheese, and codfish. They observed only a slight decrease in the viable population ranging from 0.1 to 1.6 log cycles after 57 min at —50°C. Cells of *L. monocytogenes* were more resistant to death and injury when they were inoculated in ground beef and chicken breast, whereas they were less resistant in fish. A further reduction in viability of survival cells (up to 1.0 log) was detected after 240–300 days of storage at –18°C [70].

The effects of freezing on several foodborne pathogens were reviewed by El-Kest and Marth [51]. The modes of damage to the bacterial cells were reviewed by Archer et al. [4]. The principal site of damage in

the bacterial cells during freezing has been shown to be the membrane. Very rapid cooling of cells from room temperature to —150°C resulted in more lipid crystallization before any rearrangement of intramembrane particles could occur. This leads to damage being mainly limited to the area around the cytoplasmic membrane. In slowly frozen samples, phase separation of the outer and cytoplasmic membranes was induced, causing the outer membrane to be split off by extracellular ice crystal formation. This damage could be reduced by the addition of a cryoprotectant, which modifies ice crystal formation. Damage to membranes leads to the leakage of internal cell materials, such as potassium ions, β-galactosidase, low molecular solutes, amino acids, RNA, and single- and double-strand DNA. The release of these substances has been correlated negatively with cell viability [4]. Another type of damage is osmotic dehydration of cells caused by extracellular ice formation and the resulting increase in extracellular solute concentration. This process causes the intracellular macromolecules to move closer to the membranes. The development of repulsive forces gives rise to large anisotropic stresses in the membranes, resulting in deformation, phase separation, and formation of a nonlamellar phase. Moreover, salt addition and lowered pH also play a role in the complex nature of freeze injury and cell survival [4,208].

In fermented foods, such as yogurt, frozen storage should increase the viability of beneficial cultures incorporated for their potential health benefits and control of other spoiling microorganisms. The potential beneficial roles of bifidobacteria in the human intestine reported include antagonistic effects on enteropathogenic bacteria, breakdown of carcinogenic *N*-nitrosamines, and suppression of liver tumorigenesis [100]. Thus, bifidobacteria are incorporated in dairy products. Kebary [100] studied the viability of *Bifidobacterium bifidum* in the fermented dairy product Zabady. The number of bifidobacteria surviving after 5 weeks of frozen storage (—25°C) of Zabady was higher ($>10^7$) than the minimum level necessary to achieve the beneficial effect of bifidobacteria (10^5–10^6/mL). The total bacterial count decreased as the amount of added bifidobacteria increased. This could be due to the effect of antimicrobial substances produced by bifidobacteria [100]. In eight strains of *Lactobacillus acidophilus*, higher rates and greater activity were always obtained by storing cultures at —80°C, but most strains stored at —30°C also survived well. The viability of frozen cultures was affected more by storage temperature than by cooling rate [59]. The plate counts decreased less than 1 log cycle and fermentation activity was 40%–70% when cultures of *Lactobacillus delbrueckii* subsp. *bulgaricus* were stored at —80°C for 1 year. However, fermentation activity was less than 10% when cultures were stored for 1 year at —30°C [58]. The fermentation activity of *Streptococcus salivarius* subsp. *thermophilus* was similarly reduced to 10%–60% after 1 year of storage at —30°C. Protective solutes can be used to improve survival rates.

Yeast cells in bakery products do not withstand freezing well. This can be partially compensated for by increasing the amount of yeast used in the formulation or adding improved yeast strains having a better survival rate in freezing [187]. The freeze-thaw tolerant yeast should have high trehalose content in addition to reduced activity [145]. Trehalose has been reported to perform a cryoprotectant function in the yeast cell [148]. Although the amount of yeast in the formulation could be increased, much higher levels of yeast (6%–8%) have a detrimental effect on aroma and flavor of the baked product [124]. When dough pieces were made up and frozen immediately after mixing, yeast activity remained stable after prolonged storage periods. When fermentation was allowed to proceed after mixing and before freezing, the yeast became less tolerant to freezing temperature and its activity declined. This may be due to a change in the yeast cell membrane sensitivity [92].

Physical Changes and Quality

Free and Bound Water

Different types of water are present in frozen foods. These can be broadly categorized as free and unfreezable water, which does not freeze even at very low temperatures. A major cause of product degradation is the amount of unfrozen water present in the frozen matrix. Unfrozen water is known to be reactive, particularly during frozen storage, rendering the product susceptible to deteriorative and enzymatic reactions and limiting its frozen shelf life. As given in Chapter 15, the concept of glassy state is being applied to frozen foods stability, since molecular mobility reduces the reaction rates of the unfrozen water matrix and other components [69]. Generally, unfreezable water molecules in aqueous solution are immobilized translationally or rotationally by solutes [141]. The amount of unfreezable water can be measured experimentally and mathematically computed for different types of foods.

Weight Loss

Dehydration or weight loss should be regarded as an important quality parameter for frozen unpacked foods, mainly in animal tissue. Foods lose moisture during the freezing process because their surface is exposed to heat and a moisture gradient exists within the environment [23]. Campañone et al. [23] monitored weight loss of meat during freezing and frozen storage and found a range of 0.28%–2.98% during the freezing process; meanwhile the global values (values including freezing and storage to reach up to 20 h of refrigeration) corresponded to a range between 1.67% and 6.15%. Thus, they demonstrated the importance of the surface dehydration on the meat quality.

Recrystallization

Ice recrystallization during frozen storage influences the product quality in different ways. Recrystallization of solutes and ice in frozen foods is also important to quality and shelf life. A polymer is least prone to crystallization at temperatures below glass. In general, the rate of recrystallization is highest at the midpoint between the melting and glass transition temperatures. Fluctuations in product temperature of 2°C–3°C, as are likely to be found in bulk cold stores kept at —18°C or colder, are unlikely to cause perceptible damage even over long periods [187]. However, frequent large fluctuations during retail display and during the carry-home period cause ice crystals to ripen or grow, coalesce, and move to the product surface. This leads ultimately to a freeze-dried product if packaging is permeable to moisture, allowing the sublimed or evaporated water vapor to escape. The loss of moisture results in toughening of animal tissue and greater exposure to any oxygen present.

Retrogradation

Quality loss by staling and starch retrogradation occurs most rapidly at chill temperatures in baked goods. After baking, starch from the loaf progressively crystallizes and loses moisture. Until a critical point of moisture loss is reached, freshness can be restored by heating and reabsorbing starch crystals. A tight wrap helps to keep the moisture content high for a certain amount of time. The complete crystallization of starch produces the crumbly texture of stale bread. Slow freezing is to be avoided to reduce the time spent at chill temperatures. Amylase is a useful antidote to bread staling. In general, moisture migration during frozen storage is the principal cause of staling [5,187]. It has been reported that repeated freezing and thawing treatments favored starchy paste retrogradation, which is related to a mild hydrolysis of starch chains [31].

Protein Denaturation

Some protein denaturation and solubility changes are known to occur as a result of freezing, but the practical significance of these changes is not clear [176]. Fish muscle has a unique arrangement of muscle fibers. It is divided into a number of segments called myotomes, which are separated from one another by a thin sheath of connective tissue called the myocomma or myoseptum [173]. Fish deterioration during frozen storage is associated with a decrease of protein solubility and extractability, diminishing the nutritional value [3]. Quality loss during cold storage of meat is characterized by an increase in loss of water-holding capacity, a decrease in protein extractability, a decrease in sulfhydryl groups, and a slight loss in ATPase activity [167,176]. In frozen meat, water losses are related to the denaturation of myofibrillar protein [53]. The water-holding capacity of the meat and the biochemical properties of actomyosin, such as enzymatic activity, viscosity, and surface hydrophobicity, are affected by freezing. The expressible moisture in adductor muscles increases during freezing and frozen storage. These changes are accompanied by actomyosin denaturation. The myosin and paramyosin of the actomyosin complex are most affected [150]. An amino group from some essential amino acids, such as lysine, can react with the carbonyl group of reducing sugars during processing or storage [72]. Peptides and amino acids are also increased in the drip fluid, as are nucleic acids, indicating protein changes and structural cellular damage [176]. During freezing, water molecules freeze out and migrate to form ice crystals, resulting in the disruption of the organized H-bonding system that stabilizes the protein structure, and the hydrophobic as well as the hydrophilic regions of protein molecules become exposed to a new environment. This may allow the formation of intermolecular cross-linkages either within a protein molecule or between two adjacent molecules [173].

Freezer Burn

Moisture loss by evaporation from the surface of a product leads to freezer burn, an unsightly white color that can be mistaken for mold but is resolved on rehydration during cooking unless it is severe [187]. It is usually in the form of patches of light-colored tissues, produced by evaporation of water, which leave air pockets between meat fibers [131]. Dehydration of the product or freezer burn may occur while freezing an unpackaged food item in blast freezers unless the velocity of air is kept to about 2.5 m/s and the period of exposure to air is controlled. This dehydration can be controlled by humidification, lowering of storage temperatures, or better packaging [5]. A single package of spinach and cauliflower experienced a 1.5-fold increase in loss of moisture per 2.8°C rise in temperature between —17.8°C and —6.7°C [45]. The loss of moisture occurs faster when held in a temperature cycle than when held at constant temperature during frozen storage [158].

Glass Formation

The glass transition has a dramatic effect on frozen food quality. The product is most stable below T_g', and moisture has little influence on T_g'. The presence of low molecular weight (LMW) solutes lowers the T_g', and high molecular weight (HMW) exerts little effect. This means that with increasing maturity, many vegetables display a decrease in sugars and an increase in starch, thus increasing the T_g' and the stability of frozen foods.

Functional Properties

Functional properties on any food product are normally affected by differences in freezing and thawing methods. Properties such as rheological (both flow and dynamic), textural, mechanical, consistency, appearance and sensory attributes and water-holding capacity have been correlated with freezing and thawing processes. The changes in specific functional properties become microscopically and qualitatively related to structural modifications or rearrangements of the food items. The rheological properties of fresh and frozen thawed okra dispersions were significantly different when measured at 20°C–80°C. The dispersions were pseudoplastic with both the consistency coefficient and the flow behavior index influenced by temperature. The consistency coefficient was higher for the unfrozen sample than the frozen thawed sample when measured at 20°C and 50°C, but the reverse was observed at 80°C. The flow behavior indices were not different at any temperature between 20°C and 80°C [149]. Navarro et al. [144] studied the effect of freezing rate on the rheological response of gelatinized starch pastes containing lipids. Low freezing rates increased the viscoelasticity, reduced the apparent viscosity, and led to higher structural changes of the pastes; in contrast, high freezing rates maintained the same rheological characteristics of the unfrozen samples. Graiver et al. [77] evaluated the viscoelastic behavior of refrigerated and frozen mozzarella cheese and found differences in the viscoelastic response. The storage modulus was higher for refrigerated samples in comparison with frozen cheese, in which modifications in cheese microstructure by freezing were observed with SEM methodology. Further, the freezing was correlated with casein hydrolysis, cheese matrix softening, and proteolysis acceleration.

Texture is important in frozen vegetables [63,130]. After freezing and thawing, firmness decreased, rupture strain increased, and consequently crispness decreased [62,63]. The rate of freezing was critical to tissue damage. The optimum freezing rate of carrots was established as –5°C/min using a programmable freezer and was based on texture and histological structure [61,64]. Chinese cabbage leaves cracked when frozen rapidly with liquid nitrogen. The optimum freezing rate for Chinese cabbage was 2°C/min considering tissue softening and drip loss. Freezing and thawing accelerated release of pectin, but the freezing rate did not greatly affect pectin release [63]. Fruits, such as strawberries, apples, peaches, and citrus, contain thin-walled cells with a large proportion of intracellular water, which can freeze, resulting in extensive cell rupture and radical alteration of the mechanical properties of the material [42]. Maestrelli et al. [130] studied the effect of freezing on three quality parameters of transgenic parthenocarpic (parthenocarpy produces seedless fruits) eggplants, in which the firmness of the transgenic eggplants showed a decrease. Khan and Vincent [102] studied the mechanical damage induced by controlled freezing in apple and potato. As the tissue freezes, ice crystals are formed extra- or intracellularly, pushing the cells apart or rupturing cell walls and producing large voids within the tissue.

Changes in mechanical behavior (wedge penetration, tensile, and compression) of the material were directly related to the degree of cell damage by freezing.

Mashl et al. [133] studied the unidirectional freezing of a gelatinized corn starch–water mixture and found that at freezing velocities S7.5 μm/s, starch granules were alternately pushed or entrapped by the advancing solid–liquid interface, producing a segregated structure consisting of alternating high-starch and low-starch bands. Thus, segregation of the starch within the product occurred, which is detrimental to consistency, texture, and appearance. At a velocity of 10 μm/s, the frozen product was homogeneous.

The development of rancid flavors and progressive toughening accompanied by the development of cold store flavor are the principal sensory changes in seafood [187]. Deterioration in the texture and functionality of fish tissues by frozen storage become faster than in other animal muscles [3]. The firmness of soft texture characteristic of young fish with the early onset of protein denaturation is preferred by most taste panelists [101]. Flavor change is probably more critical than texture since this can occur early [35]. The denaturation of myosin increased in a frozen solution. The rate of formation of insoluble, HMW protein aggregates increased as the temperature decreased below the freezing point and reached a maximum near the eutectic point of the solution [22]. Because of the concentration effect, pH can also change during freezing. A decrease in pH to more favorable values for degradation results in faster protein denaturation [159]. Fish gradually loses its juiciness and succulence after freezing and subsequent frozen storage. In gadoids, the chemical breakdown of trimethylamine oxide (TMAO) to dimethylamine (DMA) and formaldehyde (FA) and the subsequent cross-linking of FA to muscle proteins produced textural breakdown and resulted in a cottony or spongy texture. In this case, free water exists loosely like in a sponge. When eaten, the fish muscle loses all its moisture during the first bite, and subsequent chewing results in a very dry and cottony texture [173]. In nongadoid species, such as crab, shrimp, and lobster, muscle fibers also tend to toughen and become dry during freezing and storage.

Thawing and refreezing could lead to quality deterioration [89]. Dyer et al. [50] reported accelerated deterioration for refrozen cod fillets stored at —23°C. Changes in enzyme activities of D-glucosidase and þ-*N*-acetylglucosaminidase in rainbow trout on thawing, refreezing, and frozen storage were observed, but they did not relate to differences in sensory attributes [147]. Cowie and Little [36] reported no correlation between decreasing protein solubility and sensory attributes for cod stored at —29°C. Thawed and refrozen fish muscle displayed a faster decline in myofibril protein solubility than once-frozen fish and had reduced water-holding capacity, but analysis of proton spin-spin relaxation times indicated no changes in water location. The decline in protein solubility was not caused by complete protein unfolding. Long thawing times of 30 h before refreezing and storage resulted in cooked fish having a gray appearance and stale flavor [89]. Whole fish when thawed exhibits less textural change than filleted fish due to the presence of the backbone, which provides structural support for the flesh [173]. Gaping in fish fillet may be observed to worsen if the fish is slowly frozen. Love and Haq [125] showed that the rate at which whole cod was frozen had little effect on the gaping of the fillets cut after thawing, although very slow freezing did cause a small increase.

The functional properties of cheese, which also changed after freezing and thawing, include meltability, stretchability, elasticity, free oil formation, cohesiveness, and others. Meltability is the capacity to flow together and form a uniform continuous melted mass. Stretchability is the tendency upon pulling to form fibrous strands that elongate without breaking. Elasticity is the capacity of the fibrous strands to resist permanent deformation. Free oil formation is the separation of liquid fat from the melted body into oil pockets. Viscosity is due to particle segregation or coagulation. Luck [127] con- cluded that frozen storage was suitable for cream cheese, unripened camembert, and brick cheese, but not for gouda or cheddar cheese. Mozzarella cheese, which originated in Italy, is consumed worldwide largely due to the popularity of pizza and similar foods. Mozzarella differs from most cheeses in that it is often consumed in a melted state. Consequently, the functional properties, such as meltability, stretchability, elasticity, and free oil formation, are important to the quality of the product. Cervantes et al. [28] concluded that freezing (1-week storage) and thawing did not affect the mozzarella cheese quality as assessed by compression, beam bending, and sensory evaluation. Dahlstrom [37] showed poor meltdown, acid flavor, fat leakage, free surface moisture, bleached discoloration, and poor cohesiveness immediately after thawing, but normal characteristics reappeared after the thawed cheese was aged for 1–3 weeks. Bertola et al. [14] studied the freezing rate and frozen storage (3 months at —20°C)

of mozzarella cheese. The functional quality loss (meltability, apparent viscosity, and free oil formation) can be avoided as long as the product was aged from 14 to 21 days at 4°C before being consumed. Again freezing mozzarella cheese that had been ripened for about 14 days produced a product similar (hardness, adhesiveness, cohesiveness, springiness, and nonprotein nitrogen) to refrigerated cheese at the same stage of aging [15].

Chemical Changes and Quality

Rancidity

Oxygen is the bugbear of almost all frozen foods, leading to oxidative rancidity (if any unsaturated lipids are present), loss of color, and development of off-flavors. Freezing results in a concentration of solutes, which catalyze the initiation of oxidative reactions and disrupts and dehydrate cell membranes, exposing membrane phospholipids to oxidation. Membrane phospholipids are highly unsaturated and have been demonstrated to be the initiation point of oxidation in muscle tissue [176]. The degradation of lipids in frozen peas during storage at —18°C led to flavor damage due to the formation of hydroperoxides, thiobarbituric acid, and fatty acids, particularly in unblanched samples [84]. The lipid oxidation was mainly due to lipoxygenase and lipohydroperoxidase breakdown products [32]. The hydrolyzed and oxidized products of lipids affect the quality of frozen vegetables [169].

Oxygen availability and tissue composition play important roles in the acceleration of lipid oxidation frozen fish. Lipid hydrolysis occurs in fish during storage, which may affect lipid oxidation. Free fatty acids are believed to be more readily oxidized than the equivalent esters when lipoxygenase is involved [79,153,174]. Lipid oxidation in mackerel minces occurred continually as long as the samples were exposed to air independent of hydrolytic activity, but was deactivated or retarded by cooking the sample or by lowering the storage temperature (—40°C). Lipid oxidation was observed not only in the free fatty acids, but also in the triacylglycerides and the phospholipids extracted from mackerel mince [91]. Mincing destabilizes the fish due to a high level of incorporated oxygen and cellular disruption, making the lipids susceptible to oxidation. Most methods for frozen fish mince stabilization are based upon one or more of the following three strategies: (i) removal of prooxidants, oxygen, or components susceptible to oxidation, (ii) alternation of prooxidants, antioxidants, or other components influencing the oxidation, or (iii) addition of components that can protect fish mince lipids against oxidation [193]. Washing of fish mince helps in the removal of various antioxidative components and the relative increase in both polarity and unsaturation in the remaining lipid fraction. Heating also affects the oxidative stability of fish mince by (i) altering prooxidative enzymes, such as lipoxygenases [200], lipoxidases [103], and microsomal enzymes [182]; (ii) changing the prooxidative properties of myoglobin and other hemoproteins [29]; and (iii) enhancing the production of aqueous [200] and lipid-soluble [68] antioxidants. Undeland et al. [194] studied the lipid oxidation stability of frozen minced herring at —18°C by preheating and prewashing. Stability increased due to heat inactivation of catalytic enzymes without activation of hemoproteins. Washing reduced the stability by removing prooxidative enzymes from cooking, and reduction of antioxidants as well as a relative increase in phospholipids and free fatty acids in the fat. In case of herring fillets, the removal of the skin prior to storage at —18°C was shown to negatively affect the stability of underlying tissue. The abundance of hemoproteins, free metals, and enzymes in the under-skin layer resulted in very severe oxidative changes, especially when the fillets were stored without skin. The unfavorable composition of the under-skin layer includes a lot of dark muscle, the silver surface, the highest fat content, and the lowest level of D-tocopherol. Such local productions of oxidation products can spoil the entire flavor of the fillet; protection or removal of unstable tissues at an early stage during processing can be an important factor to improve the frozen herring storage stability [194].

Poultry fat becomes rancid during very long storage periods or at extremely high storage temperatures. Rancidity in frozen whole poultry stored for 12 months is not a serious problem if the bird is packaged in essentially impermeable film and held at —18°C or below. Danger of rancidity is greatly increased when poultry is cut up before freezing and storage because of the increased surface exposure to atmospheric oxygen [5]. Antioxidants (such as butylated hydroxyanisole (BHA), butylated hydroxytoluene [BHT], or tocopherols) and metal chelators (such as pyrophosphates, tripolyphosphates, or hexametaphosphates) are effective in reducing oxidation. The distribution of antioxidants in meat is difficult; thus, including

tocopherols in animal feed results in deposition of tocopherols in membrane locations. This is much more effective in preventing the initial step with phospholipids [176]. The frozen storage stability of antioxidant-treated beef heart surimi is reported [198,210]. Among various lipid- and water-soluble antioxidants, propyl gallate was found most protective and effective for inhibiting lipid and protein oxidation during short-term frozen storage [185]. Lipid and protein oxidation in beef surimi with propyl gallate and cryoprotectants (sucrose, sorbitol) was minimal at —70°C. Lipid and protein oxidation in frozen samples occurred with a prefreezing-thawing process before storage at —15°C and —29°C. Oxidation increased rapidly after 4 weeks. Propyl gallate inhibited lipid oxidation but was ineffective against protein changes. After 12 weeks, cryoprotectants promoted lipid and protein oxidation in the absence of propyl gallate [199].

Malonaldehyde is one of the decomposition products of autoxidation of polyunsaturated lipid materials in food. Malonaldehyde is the main component in the TBA (2-thiobarbituric acid) value that is used to evaluate the degree of oxidation of lipids. Malonaldehyde reacts with myosin from trout. The rate of reaction of malonaldehyde with D-amino groups of myosin was greater at —20°C than at 0°C and almost equal to that of 20°C [159]. Oxidant levels should be increased in frozen dough formulations, as oxidants increase dough strength. A higher shortening level is recommended for frozen dough production. Generally, shortening protects dough structure from damage owing to ice crystallization [92].

Color, Flavor, and Vitamin Loss

26.3.4.1.1 Color Loss

The most important color changes in fruits and vegetables are related to three biochemical or physicochemical mechanisms [25]: (a) changes in the natural pigments of vegetable tissues (chlorophylls, anthocyanins, carotenoids), (b) development of enzymatic browning, and (c) breakdown of cellular chloroplasts and chromoplasts. Pineapple for processing should be of optimum ripeness, with yellow color and good aroma and flavor, and free from blemishes, such as black heart, water blister, yeasty rot, or brown spot. For frozen pineapple slices, semitranslucent, highly colored slices are generally considered the most attractive and have the best flavor. Pineapple color is important because it is often the basis for judging product acceptability. The golden color of pineapple fruit is mainly due to carotenoids, which become more predominant with ripening as chlorophyll content decreases. Heat processing, freezing, and thawing lead to cell disintegration, pigment degradation, and isomerization of carotenoids [26,87,180]. Bartolome et al. [11] evaluated the influence of freezing (cold room —18°C and air-blast freezer —50°C) and frozen storage (—18°C for 0–12 months) on the color and sensory quality of pineapple slices (Smooth Cayenne and Red Spanish cultivars). No differences were found in sensory analysis (color and appearance) between the cultivars, frozen at different rates, compared with fresh product, or after 1 year frozen storage. However, both cultivars were suitable for freezing.

Color and flavor are important sensory attributes, and vitamin content is a functional attribute of frozen foods. The green color of vegetables is lost by chlorophyll degradation during freezing and frozen storage resulting from the conversion of chlorophyll to pheophytins or the destruction of both chlorophyll and pheophytins, giving a dull khaki color. During storage, chlorophyll is converted to pheophytin with a loss of green color and vitamin C; these can be used as objective indicators of quality [135,142,187].

Chlorophyll was bleached during fat peroxidation and oxidation of glycolic acid and by a-hydroxy acid dehydrogenase and chlorophyllase, which hydrolyze the phytal ester group of chlorophylls and pheophytins [190]. Storage temperature and time, acidity, and blanching time affect the loss of chlorophyll in frozen vegetables. A 10-fold increase in the conversion rate occurred with an approximate 8.3°C increase in temperature. Blanching decreased the loss of chlorophyll during frozen storage [142]. Various inorganic salts, such as sodium chloride, potassium sulfate, sodium sulfate, and sodium or ammonium bicarbonate, have been used to reduce chlorophyll loss [25].

The maximum stability of carotenes in frozen spinach was 2 years at —28.9°C, 1 year at —6.7°C, and 7 days at 4.4°C [46]. Carotene retention curves were sigmoidal with three regions: initiation, acceleration, and retardation. They were typical of autocatalytic reactions. Lipoxygenases were the major enzymes involved in carotene degradation [73]. Moharram and Rofael [142] reviewed carotene degradation in frozen vegetables. Martins and Silva [135] reported a high sensibility of chlorophylls (a and b color values) at —18°C, and results showed that color a and b values retained only 10.96% and 10.82% for chlorophylls during 60 days of frozen storage.

In poultry, a light surface color for carcasses is considered important and is best achieved with rapid surface freezing, which generates a smooth chalky white surface. This is achieved by supercooling the product and forcing nucleation of a high number of small ice crystals. These crystals stay small because there is little water migration to already formed crystals during such a fast process. Numerous small ice crystals cause the surface to reflect light and appear white in color [176]. An alternative approach is to crust freeze the outer part of the carcass rapidly using liquid brine immersion, spray systems, or cryogenics such as liquid nitrogen or carbon dioxide, and then to move the partially frozen bird to air blast or cold storage for the remainder of the process. A freezing front migration rate of 2–5 cm/h is recommended to achieve fast freezing effects and 0.1–0.2 cm/h for slow freezing [131,176].

Darkening of bones is a condition that occurs in immature chickens and has become more prevalent as broilers are marketed at younger ages. Darkening may arise during chilled storage or during the freezing and defrosting process. It occurs because some of the heme pigment normally contained in the interior of the bones of particularly young chickens leaches out through spongy areas and discolors the adjacent muscle tissues [5,176]. Leaching only occurs in carcasses from relatively young birds because the bones are not completely calcified and are more porous than in mature birds [176]. The development of dark bones was greatly reduced by a combination of freezing and storage at —35°C and immediate cooking after rapid thawing [20]. Apart from this combination, the freezing rate, time between slaughter and freezing, temperature and length of storage, and temperature fluctuations during storage have no marked influence in preventing this discoloration [5]. While taste qualities do not change, the appearance constitutes a negative factor in consumer acceptance [176].

In crustacean seafood, a dark discoloration defined as blackspot or melanosis is developed after the trauma of the capture, string, and thawing process; it is unattractive to consumers and reduces the market value. This oxidative enzyme reaction, followed by autoxidation and polymerization, may be prevented by applying sulfiting agents in combination with freezing [170]. Rotland et al. [170] carried out an experiment in which different concentrations of sodium metasulfite (included in HQ-Bacterol F), temperature and time of immersion, and subsequent freezing storage of rose shrimp were applied. They found that untreated shrimp showed melanosis after 19 h of remaining in ice and had a decreased market value at 27 h, whereas samples treated with 2% HQ-Bacterol F for 5 min maintained their market value. Further, quick freezing appeared as a good method in addition to the sulfiting agent to prevent the melanosis phenomenon, and following storage for 3 months did not affect the appearance of blackspots.

Flavor and Aroma Loss

Freezing affects the flavor and aroma of frozen foods. For example, freezing of strawberries is usually associated with a reduction in aroma and the development of off-flavor. The decrease in aroma is due to a rapid decomposition and diffusion of esters [43,49], whereas the concentrations of franeol and mesofurane linked to strawberry flavor are not affected by freezing [49]. The off-flavor of frozen strawberries differs from that of frozen vegetables [99,137,192]. Off-flavor in frozen vegetables is usually due to insufficient blanching. Deng et al. [44] found that the development of off-flavor in frozen thawed strawberries was due to the chemical production of H_2S rather than enzymatic activity. The identity of H_2S was verified both chemically and using gas chromatography–mass spectroscopy analyses. The olfactory properties by sensory analysis indicated the presence of sulfurous compounds. Usually, H_2S is derived from the sulfur-containing amino acids cysteine or methionine during processing. Deng et al. [44] also showed that amino acid was not the main precursor of the off-flavor compounds, but the off-flavor development in frozen strawberries can be attributed to the breakdown of the cells by freezing, thereby decreasing the pH in the cytosol, which in turn leads to the release of sulfide ion as H_2S. The duration of the production of H_2S was longer in strawberries at —40°C and —80°C than at —20°C. This may be due to the low boiling point of H_2S (—59.0°C). Vigorous crushing of fresh strawberries also gave rise to the production of H_2S. Thus, structural damage is one of the important factors.

In fish and seafood, FA is formed during cold storage by enzymatic decomposition of TMAO. It is a good objective criterion of time-temperature exposure in frozen gadoid species [18]. The FA reacts with proteins, thereby decreasing their solubility in salt and buffer solutions [166,187]. Santos-Yap [173] mentioned that changes in the flavor of fish and seafood generally occur in three distinct phases during frozen storage: (a) gradual loss of flavor due to the loss of or decrease in concentration of some flavor

compounds, (b) detection of a neutral, bland, or flat flavor, and (c) development of off-flavors due to the presence of compounds such as acids and carbonyl compounds that are products of lipid oxidation.

26.3.4.1.2 Vitamin Loss

Retention of nutritional components in foods is a concern when any type of preservation method is used, but freezing is probably the least destructive [176]. The destruction of vitamin C (ascorbic acid) occurs during freezing and frozen storage. This loss is influenced by blanching conditions, types of freezing, package types, and time-temperature conditions [142]. The loss is mainly due to the oxidation or to the action of ascorbic acid oxidase [169]. There is a 10-fold increase in the rate of loss of ascorbic acid per 8.9°C rise in storage temperature of frozen vegetables [13]. Generally, frozen vegetables stored at —24°C displayed better ascorbic acid retention than those at —12°C and —18°C, respectively [142]. Blanching improves ascorbic acid retention in vegetables. A combination of microwave energy and steam or water blanching yielded frozen products with better ascorbic acid retention than conventional procedures [47]. The reduction in vitamin C in frozen mashed potatoes could be overcome by the addition of encapsulated vitamin [164]. Vitamin B losses sometimes occur in frozen meat products. Vitamin B losses may be significant in frozen poultry products, but most losses are the result of the subsequent thawing and cooking treatments rather than of the freezing process [176]. Based on their studies, in which ascorbic acid and chlorophylls were measured in frozen green beans during storage, Martins and Silva [135] suggested that the shelf-life determination of frozen vegetables should importantly depend on the nutritional quality rather than only sensory attributes.

Release of Enzymes

The disruption of plant or animal tissues by freezing leads to the release of enzymes bound to the structures. Beef and pig skeletal muscle contain two isozymes of glutamic-oxalacetic transaminase: one in the mitochondria and other in the sarcoplasm [108]. Hamm and Kormendy [80] found that freezing and thawing cause a remarkable increase of glutamic-oxalacetic transaminase activity in the muscle press juice. Fish contains malic enzymes in two forms: free and latent. The latter is solubilized by the disruption of the tissue caused by freezing and thawing [76]. Barbagli and Crescenzi [7] found that the activity of cytochrome oxidase in extracts of tissues after freezing and thawing was increased by 15 times in chicken's liver, 2.5 times in trout, and 4 times in beef muscle compared to extracts of unfrozen samples. Thus, a method was developed to distinguish between fresh and frozen meat based on the enzymes released [7,75,80,81]. Around 0°C enzymatic breakdown of protein becomes the principal cause of quality loss, and below —8°C microbiological spoilage ceases and protein denaturation coupled with oxidative rancidity in fatty species becomes the chief factors affecting quality [187].

Hydrolysis

Generally, starch in vegetables does not change significantly during frozen storage [109]. Rofael [169] observed no significant changes in starch of beans, peas, okra, or mallow during storage at —18°C for 1 year. The reducing sugars of these frozen vegetables were increased during storage owing to the hydrolysis of both oligo- and polysaccharides of these products. Thus, the amount of reducing sugars is a good indicator of storage life [142]. Martins and Silva [135] found significant starch degradation rates for green bean at —6°C, —12°C, and —18°C during initial days of storage. In melons, total cell wall polysaccharides decreased more during the first 5 months than during the second 5 months of frozen storage. This suggested that pectins and hemicellulose fractions were modified and solubilized by either mechanical or enzyme-catalyzed changes in cell wall polymers [179]. However, freezing preservation of pineapple slices led to minimal changes in soluble solids and sugar content (fructose, glucose, and sucrose), pH, titratable acidity, and nonvolatile organic acids (citric and malic acids) after a year of frozen storage at —18°C [9,10].

Acetaldehyde Formation

The formation of acetaldehyde in frozen vegetables increases during storage and is thus an indication of shelf life [169]. Acetaldehyde is a product of aerobic fermentation of pyruvate in plant tissues [95]. The amount of acetaldehyde formation depends on the pretreatment, such as blanching time and storage

period [30,142,169]. Chow and Watts [30] found that acetaldehyde increased when fresh vegetables were heated beyond the minimum required for enzyme inactivation. DMA content, FA content, and shear force measurement correlated very well with sensory texture score of frozen red hake [117]. The enzymatic breakdown of triethylamine oxide to DMA and FA affects textural changes in fish species during frozen storage. Further, FA's contribution to protein changes in muscle during frozen storage would clarify the toughening mechanism. Frozen storage and fluctuation in temperature affect both DMA and FA formation in frozen fish [114].

Processing and Packaging Factors

26.3.5.1 Pretreatments for Freezing

It is important to realize that successful freezing will only retain the inherent quality present initially in a food item and will not improve quality characteristics; thus, quality level prior to freezing is a major consideration. The use of high-quality initial materials based on standards and grades is essential to high-quality frozen products. The level of intrinsic product quality, such as freshness, suitability of variety or genetics for freezing, soil nutrients for foods of plant origin, dietary factors for foods of animal origin, harvesting or slaughtering methods, and processing such as blanching, cooking, chilling, and addition of antioxidants, have also profound effects. Microbiological quality prior to freezing remains a major determinant of postthaw quality. Although freezing can reduce some pathogens, there is also usually significant survival. Thus, other methods must be used to ensure elimination of pathogenic organisms from frozen poultry [96,176]. The commonly used pretreatments are discussed in the following sections.

Blanching

Most vegetables and some fruits are blanched before freezing. Blanching destroys the permeability of cell membranes, destroys cell turgor, removes intercellular air, filling these spaces with water, and establishes a continuous liquid phase. As a result, ice crystallization can occur through the entire matrix of food without interruption during freezing process. It also affects texture, color, flavor, and nutritional quality by inactivating enzymes. Cell turgor is an important component of the eating qual- ity of many fruits. It is produced by the internal pressure of cell contents. Reduced turgor is perceived as softness and lack of crispness and juiciness. When turgor is an important product characteristic, blanching and freezing may not be acceptable. If the product is cooked before consumption, retention of turgor through earlier processing is not necessary since thermal treatment is more severe than blanching or freezing [142,167]. Blanching has also other advantages, such as destruction of microor- ganisms, and wilting of leafy vegetables assisting packaging [25]. Further, blanching favors reductions of some undesired compounds being present in some leafy vegetables, such as nitrates, nitrites, and oxalates [110]. The effect of blanching, 70°C for 15 or 30 s, and frozen storage on the stability of þ-carotene and capsanthin in red pepper was elucidated by Morais et al. [143]. Both time of blanch- ing and frozen storage were simultaneously included in two multilinear equations describing the con- centration of þ-carotene and capsanthin. There were significant differences in the decomposition rate of pigment related to cultivars and process conditions.

Properly blanched vegetables have a long shelf life at frozen food temperatures, enabling them to be exported all over the world and span the seasons [187]. Blanching of fruits may be detrimental in many cases, resulting in (a) rapid discoloration by enzymatic browning [187], (b) loss of texture, (c) formation of cooked taste, (d) some loss of soluble solids, especially in water blanching, and (e) adverse environmental impact due to energy requirements and disposal of used water [25]. Blanching at 70°C–105°C is associated with the destruction of enzyme activity. Hot-water blanching is usually carried out between 75°C and 95°C for 1–10 min, depending on the size of the individual vegetable pieces. High-pressure steam blanching is more energy efficient than water blanching. It is important that cooling be carried out shortly after blanching, especially for products to be frozen [25].

The enzymes involved in the production of off-flavor are catalase, lipoxygenase, and peroxidase, and their heat stability varies with the types of vegetables and fruits. Peroxidase and catalase seem to be the

most heat stable; thus, they could be used as an index of adequate blanching for vegetables. A 95% loss of enzyme activity following blanching is considered adequate. The quality of blanched frozen vegetables was improved if some peroxidase activity remained at the end of the blanching process. The activities of most enzymes are greatly dependent on pH of the tissue or the blanching water. Additives, such as citric acid, sodium chloride, and carbonates, can be used in water depending on the purpose [25,34,142]. Bottcher [19] reported that the highest-quality products were obtained when the following percentages of peroxidase activity remained: peas, 2%–6.3%; green beans, 0.7%–3.2%; cauliflower, 2.9%–8.2%; and brussels sprouts, 7.5%–11.5%. It was concluded that the complete absence of peroxidase activity was indicated over blanching [25].

Heat Treatments

Texture is an important quality attribute of frozen fruits and vegetables. Loss of tissue firmness, disruption of the cell membrane, and excessive softness are the major consequences to be avoided [162]. Low temperature and long-time pretreatment were useful in improving the texture of frozen vegetables by avoiding excessive softness. Carrots heated for 30 min at 60°C and frozen above —5°C/min (optimum rate) should escape both cell damage and excessive softening [61,114,188]. The deesterification of pectin by pectin methylesterase during preheating prevented transelimination of pectin [8,60,116,160]. Fuchigami et al. [65] found that preheating followed by quick freezing was effective in improving excessive softness and cell damage. The optimum preheating occurred with 30 min at 60°C or 5 min at 70°C, and the optimum freezing was —5°C to —50°C. Preheated carrots retained a firmer texture than those blanched in boiling water. After preheating, the amount of high methoxyl pectin decreased and low methoxyl pectin increased. Quick freezing process resulted in better texture than slow freezing. Loss of texture was accompanied by the release of pectin. Slow freezing accelerated the release of pectin as compared to quick freezing. Preheated carrots were slower to release pectin. The degree of esterification of pectin substances in raw carrots decreased during preheating, freezing, and thawing. Cell damage in quick-frozen carrots was slight. Product preparation prior to freezing may include cutting, deboning, slicing, and other operations to provide greater convenience. A greater variety of products cooked prior to freezing is becoming popular with consumers. These include breaded and fried portions, cured and smoked products, and items in marinades or broths [176]. The freezing rate of precooked chicken affects the quality of the product. Breaded precooked drumsticks frozen with liquid nitrogen are susceptible to cracking, separation of meat from the bone, and developing small areas of white freezer burns next to the surface [5]. Cooked products are likely to exhibit greater increases in lipid oxidation than raw products during storage. This is due to the oxidative change and higher TBA values making the product more susceptible to further oxidative changes during frozen storage. Antioxidants are very effective in cooked chicken during frozen storage [94,114,156,202].

Dipping Pretreatments

In many cases, foods are dipped or soaked in different solutions before freezing and the type of solute used depends on the desired purpose. Apple slices are commonly treated by soaking it in 1% salt solution to remove intercellular air. Fruits are also dipped in ascorbic acid and sugar solutions to minimize browning or blanched for a short time to inactivate enzymes [167]. Paredi et al. [150] studied the effect of dipping in polyphosphates on the biochemical properties of adductor muscles when frozen and stored at —30°C. Immersion in polyphosphates solution was effective in reducing water loss in stored muscle. In addition, it delayed the decrease in enzymatic activity (Mg^{2+}-ATPase) and provided some protections for the myosin light chains without affecting either the extractability or the viscosity of actomyosin from frozen stored muscles.

In many cases, the frozen product is protected by a suitable glazing compound. A glaze acts as a protective coating against the two main causes of deterioration during storage: dehydration and oxidation. It protects against dehydration by preventing moisture from leaving the product, and against oxidation by mechanically preventing air contact with the product. Oxidation can also be minimized if the glaze carries a suitable antioxidant [5]. For products intended for short-term storage, glazing can be practically utilized as a viable alternative to storage without a protective covering [173]. Moreover, glazing treatment could be a cheaper alternative to expensive packaging systems for fish stored at —20°C [93]. The different glazes available include inorganic salt solutions of sodium acid phosphate, sodium carbonate, and calcium lactate,

alginate solution (also known as *Protan* glaze), antioxidants (such as ascorbic and citric acids, glutamic acid, and monosodium glutamate), and other edible coatings (such as corn syrup solids) [205].

Bacterial Ice Nucleators or Antifreeze Proteins

The application of bacterial ice nucleators to the freezing of some model food systems and real foods (such as salmon, egg white protein, and cornstarch gels) elevates nucleation temperatures, reduces freezing times, and improves the quality (such as flavor and texture). These can also be used in freeze concentration of fresh foods for modification of their properties [201]. The use of bacterial ice nucleators is a unique application of biotechnology, as it directly improves freezing processes [118]. When bacterial cells were added to isotropic aqueous dispersions of hydrogels composed of proteins and polysaccha- rides, the bulk of the water was converted into directional ice crystals at subzero temperatures not lower than —5°C, and resulted in the formation of anisotropically textured products [118]. Details of this topic are reviewed by Wolber [207] and Li and Lee [118]. Antifreeze proteins, found in polar fish and cold-tolerant insects and plants, can affect freezing in several different ways: (a) by lowering the freezing temperature, (b) by retarding recrystallization on frozen storage, and (c) by promoting ice nucleation causing supercooled solutions to freeze more rapidly [69,74]. Mizuno et al. [141] studied the effect of solutes on the antifreeze and immobilizing activities of water. The antifreeze activities of saccharides that consisted of glucose were higher than others, and in salts those that possessed a higher ionic charge had higher antifreeze activities. In water-soluble amino acids, a few amino acids that formed no eutectic mixture above —20°C had especially high antifreeze activities. The high antifreeze activity is caused by immobilizing activity for water molecules, and the immobilizing mechanism varied with the type of solute [141]. The antifreeze proteins depress the freezing point by attaching to ice crystals and interfering with water molecules joining the ice lattice. Computer modeling suggests that at least for one antifreeze peptide, the molecules are arranged in an antiparallel fashion with cooperative side-to-side binding [121]. There are two groups of antifreeze proteins: antifreeze glycoproteins and antifreeze proteins. The primary structure of the antifreeze glycoproteins is a repeating (Ala-Ala-Thr) sequence with a disaccharide attached to the threonine residue. The antifreeze proteins have various structures. Type I proteins have an D-helical structure, whereas type II and III proteins have some unusual secondary structures. Synthetic antifreeze peptides may have also practical applications in foods [121]. In a recent report, it is mentioned that phenomenon of cold acclimation in carrots was related with biochemical and physiological changes in the fresh plant [74]. The presence of antifreeze protein within the roots was related to cold acclimation and its quality enhancement through freezing.

26.3.5.1.1 Osmotic Concentration

Partial removal of water by osmotic treatment to freezing is recognized as convenient for reducing cellular damage of fruits and vegetables, which causes softness after thawing [183]. Osmotic concentration of vegetables prior to freezing is a pretreatment that can improve final product quality [25,183]. It is well established that osmotic dehydration improves the product quality in terms of color, flavor, and texture. The merits of osmotic dehydration for product-quality improvement and process efficiency were reviewed earlier [161,163,191]. The effects of sugar on the quality of frozen fruits have been reviewed by Skrede [181]. However, in the literature there is not much fundamental information about the mechanisms of flavor entrapment in the food matrix, color retention, and physics of textural improvement. In the frozen food industry, high energy levels are used for freezing because a large quantity of water is present in fresh foods. A significant proportion of this energy could be saved if plant materials were concentrated prior to freezing [90]. A reduction in the moisture content of food can reduce refrigeration load during freezing. Partially concentrating fruit and vegetables prior to freezing saves packaging and distribution costs [17]. The product quality is comparable with that of conventional products. The process is referred to as dehydrofreezing.

26.3.5.1.2 Cryoprotection

Meat and fish muscle is susceptible to freeze denaturation, which decreases gel-forming potential, water-holding capacity, and protein solubility. Cryoprotectants are generally added to protect fish myofibrillar proteins from freeze denaturation during frozen storage [152]. Polydextrose, sucrose, and sorbitol have

been reported to protect against freeze denaturation of Alaskan pollack surimi [151]. These are low in cost, safe, and have good solubility and beneficial functional effects [107,128]. Sucrose is usually combined with sorbitol to reduce sweetness. The cryoprotective effect of sugar is enhanced by adding polyphosphate [115]. Polydextrose proved to be an effective cryoprotectant for both pre- and postrigor beef. Arakawa and Timasheff [6] found that cryoprotectants increase the surface tension of water as well as the binding energy, preventing withdrawal of water molecules from the protein and thus stabilizing the protein. Phosphates had no cryoprotective effect but did increase pH and enhanced protein extractability, which may enhance gel-forming and water-holding properties [131].

Park et al. [152] found that cooked gel strength was unaffected by freezing of beef or pork surimi-like materials for 48 h, and addition of cryoprotectants (3% or 6% sorbitol, 3% glycerol, or 3% sucrose) before freezing had no effect on gel-forming ability. The washed myofibrillar proteins from beef muscle were quite stable during freeze-thaw treatment up to 6% sodium chloride. No difference in gel-forming ability after freezing with or without added salt was found. Wierbicki et al. [206] also reported no detrimental effects on water-holding capacity due to salting of meat prior to freezing. The interaction between salt ions and muscle proteins occurs rapidly, compared to the normal process of shrinking or coagulation of muscle proteins [39]. Dondero et al. [48] studied the cryoprotective effects of 18, 20, 25, and 36 DE (dextrose equivalents) maltodextrins at 8% (w/w) in surimi from jack mackerel stored at —18°C for 27 weeks. They found that 20 and 25 DE maltodextrins as well as sucrose or sorbitol mixtures were most effective in stabilizing surimi proteins during frozen storage [48].

Poultry meat showed little deterioration upon freezing and isolated myofibrillar systems made by the surimi procedure are less stable [128]. Kijowski and Richardson [104] found that mechanically recovered meat from broilers had reduced functionality when no cryoprotectants were used. Sorbitol or sucrose showed some protection of gel-forming ability of frozen samples, and sorbitol or sucrose with tripolyphosphate gave stronger gels after freezing or freeze drying than fresh samples. The combined presence of sorbitol, sucrose, and tripolyphosphate restored most functional properties of frozen or freeze-dried material to that of the fresh material. Most of the loss of functionality during freezing or freeze-drying was caused by the loss of solubility of myosin and, to a lesser extent, actin. Freeze drying had a greater effect when no additive or NaCl was present. The blast-frozen and freeze-dried samples with no cryoprotectants had a very coarse structure with no obvious fine network system. In the presence of sorbitol or sucrose, there was a finer meshwork for freeze-dried material, which was finer for frozen material. In the presence of sorbitol or sucrose with tripolyphosphate, the network was even finer but with less obvious spaces in the matrix for both freeze-dried and frozen material. These were observed by scanning electron microscope.

Whole egg and yolk products are fortified with salt or sugar before freezing to prevent coagulation during thawing. The selection of additive depends upon the finished product specifications. Salt (10%) is added to yolks used in mayonnaise and salad dressings, and sugar (10%) is added to yolks used in baking, ice cream, and confectionary. Egg whites are not fortified as they do not have gelation problems during defrosting [5]. Table 26.1 shows the effects of freezing on the functional properties of liquid egg products. HMW polymer cryoprotectants have the following advantages over LMW cryoprotectants [105]:

1. HMW polymers do not generally penetrate the cell membrane and remain in the extracellular suspensions and /or outer surface of the cell.
2. HMW polymers do not produce a significant freezing point depression within the range of concentrations that can be applied in practice.
3. There is no binary eutectic effect, i.e., the hydrated polymer does not crystallize from aqueous solution as LMW agents do.
4. HMW polymers have the ability to keep a substantial portion of the solution from freezing.

Although the presence of HMW polymeric cryoprotectants is limited to the extracellular suspension medium, HMW additives affect the intracellular composition by the efflux of intracellular water due to chemical potential change across the membrane when extracellular ice is formed [105].

TABLE 26.1

General Effects of Freezing Rate, Storage Time, Storage Temperature, Thawing Rate, and Additives on Functional Properties of Liquid Egg Products

	Effect on Functional Properties		
Factor	**Egg Albumen[a]**	**Egg Yolk[b]**	**Whole Egg[c]**
Freezing rate	Slower rate causes: reduced viscosity and increased foam stability	Slow rate causes: increased viscosity and gelation	Same as liquid egg yolk but less severe
Storage time	Longer time causes: reduced viscosity and increased foam stability	Longer time causes: increased viscosity and gelation	Same as liquid egg yolk but less severe
Storage temperature	Lower temperature causes: reduced viscosity and increased foam stability	—18°C results in maximum increase in viscosity and gelation	Same as liquid egg yolk but less severe
Thawing rate	Faster rate causes: some protein denaturation	Slower rate causes: increased viscosity and gelation	Same as liquid egg yolk but less severe
Additives	None normally needed	2% NaCl and 8% sucrose inhibit gelation; 10% used commercially	None normally needed

[a]Freezing usually has only a slight effect on egg albumen properties.
[b]Freezing often has a drastic effect on egg yolk viscosity.
[c]Freezing has a greater effect on whole egg properties than albumen but less than the effect on egg yolk.
Source: P. L. Dawson, *Freezing Effects on Food Quality* (L. E. Jeremiah, ed.), Marcel Dekker, New York, 1996, p. 337.

26.3.5.1.3 Irradiation

High-dose irradiation can produce changes in the chemical composition and taste of fish and seafood. A combination of irradiation and freezing can be used in foods. A combination treatment involving freezing in conjunction with irradiation has recently been proposed as a means of retarding spoilage. It has been reported that some European countries irradiated frozen seafoods from Asia to eliminate microbial pathogens such as *Salmonella* [172].

Storage and Display

Packaging, storage, and display also affect the frozen food quality. Loss of quality in frozen foods is a gradual process; the changes being slow or very slow, cumulative, and irreversible [187]. Optimum quality requires care in every stage of processing, packaging, storage, and marketing sequence. Storage temperature is important for frozen food. Symons [187] mentioned that the speed of freezing was not as important to product quality as the maintenance of adequately cold temperatures (—18°C or less) during distribution. A package for frozen product should (a) be attractive and appeal to the consumer, (b) protect the product from external contamination during transport and handling, and from permeable gases and moisture vapor transfer, (c) allow rapid, efficient freezing and ease of handling, and (4) be cost effective. To provide the greatest protection, a package must be well evacuated of air (oxygen) using a vacuum or gas-flushed system and provide an adequate barrier to both oxygen and moisture [5,176]. Since cost is involved in vacuum or modified-atmosphere packaging, these should be used when necessary for quality. For example, vacuum packaging need not be used if lipid oxidation is not the limiting factor affecting the shelf life of a product.

The shelf life of frozen foods kept in open display cabinets at —15°C packed in 23 different types of plastic, cardboard, and laminate was studied. It was found that aluminum foil-laminated and metallized packages gave the best results. This is due to low levels of oxygen permeability, water vapor transmission, and light transparency, and less fluctuating temperatures [2]. Two terms used to describe the shelf life of frozen foods are practical storage life (PSL) and just noticeable difference (JND). PSL is the level of quality expected for the product by the ultimate consumer. JND is usually determined by a trained taste panel,

and then multiplied by an arbitrary figure, generally between 2 and 5, to arrive at a PSL [187]. In some sensitive products, such as peaches, cauliflower, red-pigmented fish, the PSL may be close to the JND [187]. Most frozen products enjoy a shelf life of many months or even years [187].

Quality losses of frozen food increase log linearly with the storage temperature when greater than —18°C [113]. The rate of quality loss increases about 2–2.5 times for every 5°C increase over —18°C [72,111,112]. In poultry, it has been suggested that shelf life is likely to change by a factor of 3.5 for each 10°C change, up or down [176]. In seafood kept at around 0°C, enzymatic breakdown of protein becomes the main cause of quality loss, below —8°C microbiological spoilage ceases, and protein denaturation coupled with oxidative rancidity in fatty species becomes the chief factor affecting quality [168, 187]. Some types of foods, such as fish, pork, animal organs, fried chicken, and spinach, can be maintained in a high-quality state for only 3–7 months at —20°C, whereas other foods, such as beef, sugared fruits, many bakery products, and many vegetables, can be maintained in a high-quality state for more than 12 months at —20°C [54]. Fish stored at —29°C will have a shelf life of more than a year [5]. Some PSL values determined by the International Institute of Refrigeration (IIF) are reported by Symons [187].

Thawing

Thawing as a final and obligatory step of the freezing process is quite important. Thawing properly is essential to maximize quality retention and safety of frozen foods. Microbiologically safe thawing process includes: (a) inside a refrigerator at temperatures below 5°C, (b) microwave oven, or (c) as part of the cooking treatment [135]. Although thermal processing in microwave and cooking assures a better microbial destruction when compared with thawing inside a refrigerator, sensory retention is compromised. In a study on green beans' quality loss upon thawing, Martins and Silva [135] found that sensory parameters, such as flavor and color, were more sensitive to thawing at refrigeration temperature (3°C–7°C) than nutritional properties, such as vitamin C and starch contents. In a study of Virtanen et al. [197], the thawing time of a model food system based in wheat flour was reduced to a seventh part, when they combined microwave energy and cold air in comparison to convective thawing at ambient temperature, but no quality changes were quantified. High-pressure, microwave, ohmic, and acoustic thawing are innovative applications that are being explored to improve the con- ventional thawing methods. High pressure preserves food quality and reduces the necessary time for thawing; but some inconvenient characteristics have been mentioned, such as high costs, protein denaturation, and meat discoloration [119]. Similarly, microwave, ohmic, and acoustic thawing may require shorter thawing times, but some limitations have been found. Heterogeneous heating, con- trolled frequencies, and much more investigations need to be considered with these new thawing methods [120].

Cold Chain Tolerance and Quality

26.3.6.1 Temperature Cycling

The steps in the frozen food cold chain are freezing, transport by refrigerated vehicle or container, distribution store, retail display cabinet, the unrefrigerated period between retail outlet and home, and time in a home freezer before being consumed in the frozen state, thawed or end cooked. Temperature abuse at any of the above steps causes quality deterioration. Time-temperature indicators have been proposed to monitor the lack of adequately cold temperatures during the cold chain. Fluctuations in storage temperature may contribute to deterioration of frozen foods [142].

26.3.6.2 Time-Temperature Tolerance Indicators

The concept of time-temperature tolerance (TTT) to describe frozen food stability is important. Physicochemical, chemical, or biological reactions give an irreversible indication (usually visible) of the history of the product. These indicators are placed on the outside of the packages and combine the time and temperature conditions to which they have been exposed [25]. Temperature history indicators do not provide a precise record of temperature as it changes with time, as do time-temperature recorders or digital data acquisition systems, but are less costly [203]. Indicators that respond

continuously for all temperature conditions are said to be full-history indicators, whereas devices that respond only for the period of time during which a temperature threshold has been exceeded are called partial-history indicators [204]. More detailed review of time-temperature indicators is given by Taoukis et al. [189]. The applicability and effectiveness of time-temperature integrators (TTI) as monitors and controlling tools for frozen chain and distribution of frozen vegetables, green peas, and mushrooms were assessed by Giannakourou and Taoukis [71]. In this analysis, TTI response provided a reliable indication of the relative quality status of the frozen products, in which these TTI tools may be utilized as base to optimize the management system and consequently to improve con- sumer acceptance [71].

26.4 Freezing Methods

The overall cost of freezing preservation is lower than that of canning or drying if the freezer can be kept full [82]. If the material enters the freezer at just above the freezing point, a more controlled crys- tallization occurs compared to material at ambient temperature. Different types of freezing systems are available for foods. No single freezing system can satisfy all freezing needs because of a wide variety of food products and process characteristics [88]. The selection criteria of a freezing method are the type of product, reliable and economic operation, easy cleaning ability, hygienic design, and desired product quality [5]. Although all commercial freezing processes are operated at atmospheric condi- tions, there are potential applications of high-pressure assisted freezing and thawing of foods. The pressure-induced freezing point and melting point depression enables the sample to be supercooled at low temperature (e.g., —22°C at 207.5 MPa), resulting in rapid and uniform nucleation and growth of ice crystals on release of pressure. Other results include increased thawing rates, the possibility of non- frozen storage at subzero temperatures, and various high-density polymorphic forms of ice [97]. Details of the applications of this process are reviewed by Kalichevsky et al. [97]. In the food indus- try, plate contact, immersion, air blast, fluidized-bed, and cryogenic freezing are common methods. The freezing rate in these methods is achieved by controlling the convective or surface heat transfer coefficient with a typical range of 5–2000 W/m^2 K [196]; and the thermal conductivity of foods ranged from 0.5 to 1.5 W/m K [186]. On the other side, heat to be removed from the foods (i.e., refrigeration load) mainly depends on the specific heat and latent heat. Some data of these important physical prop- erties are included in Table 26.2 [27,195,196].

26.4.1 Freezing by Contact with a Cooled Solid: Plate Freezing

In this method, the product is sandwiched between metal plates and pressure is usually applied for good contact. Plate freezers are only suitable for regular shaped materials or blocks. When the product has been frozen, hot liquid is circulated to break ice seal and defrost. Spacers should be used between the plates during freezing to prevent crushing or bulging of the package.

26.4.2 Freezing by Contact with a Cooled Liquid: Immersion Freezing

In this method, food is immersed in a low-temperature brine to achieve fast temperature reduction through direct heat exchange [88]. The fluids usually used are salt solutions (sodium chloride), sugar solutions, glycol and glycerol solutions, and alcohol solutions. The solutes used must be safe to the product in terms of health, taste, color, and flavor, and the product must be denser than fluids. Dilution from the foods may change the concentration, thus it is necessary to control the concentration to maintain a constant bath tem- perature. To ensure that the food does not come into contact with liquid refrigerants, flexible membranes can be used to enclose the food completely while allowing rapid heat transfer [69]. The water loss and salt gain, were less than 2 and 1 g /100 g respectively of the initial gelatin gel in immersion freezing with sodium chloride solution. The salt penetration was hindered by formation of an ice barrier [126]. A mix- ture of glycerol and glycol is liquid–liquid medium, thus it can also be used since there is no eutectic point. As the temperature is lowered, a point is reached where ice crystals are formed as slush. The temperature

TABLE 26.2

Physical Properties of Some Freezing Systems and Food Products

	Typical Surface Heat Transfer Coefficient and Foods Thermal Conductivity		
Freezer Type	**Conditions**	***h* (W/m^2 K)**	**Example Foods Preserved by the Method**
Cold room	Still air	5–10	Beef carcass, chicken, fruits, vegetables.
Air-blast	Air velocity: 2.5–5 m/s	15–30	Fruits, vegetables, fish fillets.
Tunnel	Counterflow of food item and air	15–60	Grains, soybean, fish fillets.
Fluidized-bed	Suspending airstream	80–120	Carrot cubes, peas, shrimp, strawberries.
Plates	Contact to solid	50–120	Meat steaks, fish fillets, leafy vegetables.
Cryogenic	Gas zone/spray zone	40–60/100–140	Ice cream, shrimp, berries.
Liquid immersion	Circulating brine	60–90	Chicken, turkey, canned foods.
	Specialized refrigerant	500–1200	Fruits, tomato slices, orange segments.

Food Item	***k* (W/m K)**	**Cp above and below Freezing (kJ/kg K)**		**Latent Heat of Fusion (kJ/kg)**
Apples	0.513 (before freezing, water 84.9%)	3.65	1.90	281
Bananas	0.481 (before freezing, water 75.7%)	3.35	1.78	251
Chicken		3.32	1.77	247
Ice cream	0.460 (before freezing, at 0°C)	2.95	1.63	210
Milk (whole)	0.473 (before freezing, water 87.0%)	3.79	1.95	294
Oranges	0.580 (before freezing, water 85.9%)	3.75	1.94	291
Shrimp	0.490 (before freezing, water 75.3%, fat 1.2%)	3.62	1.89	277
Strawberries	0.462 (before freezing/1.125 (at —15.5°C)	3.86	1.97	301
Tomato (ripe)	0.571 (before freezing, water 92.3%)	3.99	2.02	314
Turkey	0.343 (before freezing, water 92.8%, fat 12.4%) 1.437 (water 92.8%, fat 12.4%, at —9.4°C) 1.627 (water 92.8%, fat 12.4%, at —23.3°C)	2.98	1.65	214
Water	0.594 (before freezing, at 0°C)	4.23 (at 0°C)	2.01	334
Watermelon	0.571 (before freezing, water 92.8%)	3.96	2.01	311

at which slush ceases to flow is called the flow point. Methanol or ethanol can also be used. Although the methanol will be removed during cooking, it is poisonous whereas ethanol is safe. Alcohols also pose a fire hazard in processing plants.

26.4.3 Freezing by Contact with a Cooled Gas

26.4.3.1 Cabinet Freezing

In this method, cold air is circulated in a cabinet where product is placed in a tray. The moisture pick-up from the product surface may deposit on the cooling coils as frost, which acts as an insulation. A cabinet freezer with air velocity at least 5 m /s generates high heat-transfer rates [88].

26.4.3.2 Air-Blast Freezing

In this method, the temperature of food is reduced with cold air flowing at a relatively high speed. Air velocities between 2.5 and 5 m/s give the most economical freezing. Lower air velocities result in slow product freezing, and higher velocities increase unit-freezing costs considerably [5]. This method can be further divided into tunnel freezing, belt freezing, and fluidized bed freezing, depending on how air interacts with the product [88].

26.4.3.2.1 Fluidized Bed Freezing

A fluidized bed freezer consists of a bed with perforated bottom through which refrigerated air is blown vertically upward. The air velocity must be greater than the fluidization velocity. This freezing method is suitable for small particulate food bodies of fairly uniform size, e.g., peas, diced carrots and potatoes,

corns, and berry fruits. The high degree of fluidization improves the heat-transfer rate and results in good use of floor space.

26.4.3.2.2 Belt Freezing

The first mechanized air-blast freezers consisted of a wire mesh belt conveyor in a blast room for continuous product flow. Uniform product distribution over the entire belt is required to achieve uniform product contact and effective freezing. Controlled vertical airflow forces cold air up through the product layer, thereby creating good contact with the product particles and increasing the efficiency. The principal current design is the two-stage belt freezer. Temperatures used usually are —10°C to —4°C in the precool section and —32°C to —40°C in the freezing section [5].

26.4.3.2.3 Spiral Freezing

A spiral belt freezer consists of a long belt wrapped cylindrically in two tiers, thus requiring a minimal floor space. The spiral freezer uses a conveyor belt that can be bent laterally. It is suitable for products with a long freezing time (generally 10 min to 3 h), and for products that require gentle handling during freezing. It also requires a spatial air-distribution system [5].

26.4.3.2.4 Tunnel Freezing

In this process, products are placed in trays or racks in a long tunnel and cool air is circulated over the product.

26.4.4 Cryogenic Freezing

In cryogenic freezing, liquefied gases are placed in direct contact with the foods. Food is exposed to an atmosphere below —60°C through direct contact with liquid nitrogen or liquid carbon dioxide or their vapor [88]. This is a very fast method of freezing; thus, adequate control is necessary for achiev- ing quality products. It also provides flexibility by being compatible with various types of food prod- ucts and having low capital cost [69]. The rapid formation of small ice crystals greatly reduces the damage caused by cell rupture, preserving color, texture, flavor, and nutritional value. The rapid freez- ing also reduces the evaporative weight loss from the products, provides high product throughput, and has low floor space requirements [69]. Thermal diffusivity of the food will, however, restrict the heat transfer of heat from the product to the freezing medium [69]. Cryogenic gases can also be advanta- geously applied to produce a hard, frozen crust on a soft product to allow for easier handling, pack- aging, or further processing [122]. The cryomechanical technique utilizes a cryogenic gas to create a frozen crust on a fluid product, after which the product may then be conveyed to a conventional mechanical freezer. Combination of these processes offers advantages of both systems [69]. The advantages of liquid nitrogen are that it is colorless, odorless, chemically inert, and boils at —195.8°C [177]. It is usually used for high-value products due to the high capital cost for gas compression. The product can be exposed to a cryogenic medium in three ways: (a) the cryogenic liquid is directly sprayed on the product in a tunnel freezer, (b) the cryogenic liquid is vaporized and blown over the food in a spiral freezer or batch freezer, or (c) the product is immersed in cryogenic liquid in an immer- sion freezer [78,177].

26.5 Emerging Freezing Techniques

Some new freezing techniques or combinations are being developed for their potential benefits, technical and economical advantages, and quality enhancements. Several kinds of high-pressure ices with different chemical structures and physical properties are reported [57,86]. A pressure-shift or high-pressure freezing process can generate small and uniform ice crystals [119,211]. Improved

structures by pressure-shift freezing are reported for tofu (soybean curd) [67,98] and carrots [66]. In case of the tofu, the texture was almost same for pressure above 200 MPa as in the case of the untreated tofu [67]. Similarly, in case of carrots above pressure 100 MPa, the damage could be reduced significantly [66]. The freezing point of water from 0°C at 101.3 kPa can be shifted to —21°C under 2.1×10^5 kPa [211]. Zhu et al. [211] carried out a comparative study on pork muscle applying pressure-shift, air-blast, and liquid-immersion freezing methods. They found differences in size and distribution of ice crystals and consequent muscle damage, in which the pressure-shift freezing prevented the muscle disruption. A cryomechanical or combined freezing with cryogenic freezing followed by air-blast freezing was utilized to improve frozen food product quality. It is recommended for delicate products with poor mechanical resistance, such as shrimp, raspberries, strawberries; or chicken and mushrooms when significant changes occurred in the product [1]. In this combined process, a protective crust is formed through the immersion in the liquid N_2, which is characteristic of the products. A dehydrofreezing method is a combined method of a controlled dehydration previously to the freezing stage, which is mainly promising for fruits and vegetables preservation due to the high moisture content. This technique reduces refrigeration loads and packaging, storage, and distribution costs; and provides a comparable quality [119].

26.6 Addition to Hurdle Technology

Freezing process can be used as one of the hurdles in combined methods of food preservation. Piotrowski et al. [157] carried out a study with osmotic dehydration, freezing, and microwave convective drying to preserve strawberries. In case of apple cubes, an osmotic dehydration treatment followed by freezing provided good quality and acceptance. The optimum conditions were found to be 55°Brix, 35°C for the solution, and 60 min of osmotic dehydration time with a fast freezing [21]. Sun and Li [186] and Li and Sun [120] applied ultrasound with freezing to potato tissues, which resulted in an improved freezing rate. Higher freezing rates produced better cellular structure, less intercellu- lar void formation, and less cell disruption when studied by cryoscanning microscopy analysis. The application of power ultrasound was effective in improving the structure of frozen-then-thawed potatoes. A combination of dehydration in concentrated solutions and freezing was applied to muskmelons [129] and strawberry slices [183] to identify improvement in texture and structure. Moisture reduction of muskmelon, prior to the freezing process, improved the quality by reduction in the exudates' loss and texture after thawing [129]. Also after thawing, the predehydrated strawberry samples exhibited a better tissue organization than the frozen slices without pretreatment, being the best texture that cor- responded to air-dried and the osmotic concentrated–air-dried strawberry samples [183]. Fagan et al.
[52] utilized a modified-atmosphere packaging, with different N_2 /CO_2 ratios, combined with freeze chilling to extend the shelf life of raw whiting, mackerel, and salmon, finding that these combined technologies confer logistic benefits not only during frozen storage but also in product distribution and retailing.

26.7 Future Research in Freezing Process

Further research needs to be targeted in the following areas: (i) heat and mass transfer phenomena involved during freezing, storage, and thawing; (ii) measurement and prediction of food properties during freezing and thawing, such as enthalpy changes, convective heat transfer coefficients, nutrient, and quality kinetics; and (iii) prediction of freezing and thawing time, and freezing rates. Concepts based on engineering principles, mathematical knowledge, and modeling as well as computer simulation need to be included as part of a good process development, equipment design, and optimization of food freezers. Quality kinetics need to be included in optimization of freezing process. A short list of studies related to the aforementioned engineering aspects is presented in Table 26.3. Implementing hazard analysis and critical control point, and compliance with all aspects of good manufacturing practice could be properly applied to ensure the quality and safety of frozen foods.

TABLE 26.3

Engineering Concepts Importantly Related to Freezing Process, Frozen Storage, and Thawing

Engineering Concept	Comment	Tested Food	Reference
Freezing time	Combination of plank and unsteady heat transfer equations	Beef	[136]
Freezing time	Comparison of existing approaches, analytical and numerical	Strawberries	[83]
Freezing and thawing times	Experimental and predicted freezing and thawing times	Lean beef	[33]
Thermophysical properties	Computer program developed to predict freezing and thawing	Codfish	
Freezing and thawing times	times: Method based on enthalpy formulations	Peas	[132]
Freezing and thawing times	Analytical method developed for high water foods	Fishes, meats	[171]
Properties, freezing time, and heat load	Prediction of enthalpy–temperature curves of foods over a range —40°C to 40°C	Cheese, fish, fruits, meats	[155]
Enthalpy and properties	Industrially processed food materials except fatty foods	Lean beef	[56]
Freezing processes	Update of freezing time predictive models based on heat	Meat balls	
Weight loss kinetics	Mathematical model based on heat and mass balances, and mass transfer phenomenon	Meat, potato Beef	[24] [41]
Freezing and thawing times	Comparison of predictive models with experimental data	Fish, potato	[123]
Thermal-physical properties	Experimental and computer properties' comparison	Green peas	[134]
Heat transfer rates and	Numerical model based on energy equation with the	Beef, egg	
Enthalpy change	Navier–Stokes equations		[85]
Quality loss kinetics	Computational evaluation of frozen quality profile	Green beans	[135]