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Packaging Materials and Technologies for Improving Quality of Frozen Foods

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ABSTRACT

Quality of frozen foods is influenced by various factors including freezing operation, storage temperature, food components and packaging systems. Packaging materials e.g. PE, nylon, PET, etc. and packaging atmosphere surrounded foods have key role on quality changes of frozen products. This paper aims to review utilization of packaging materials and technologies applied in frozen foods to improve and monitor quality of frozen products. The principles of phase transition in freezing process and glass transition which affect quality deterioration of frozen foods are explained. Migration of water, i.e. ice recrystallization and water loss from foods is the major problem found in all frozen products. Several biochemical reactions during frozen storage are limited, however, take place and are accelerated during thawing e.g. lipid and protein oxidation, enzymatic reaction and microbial activity leading to loss of quality and safety. Developed packaging technologies i.e. modified atmosphere packaging, edible film/coating, active and intelligent packaging utilization and consequence on frozen food qualities are discussed. The appropriate selection of packaging materials and operations can minimize changes and improve quality of frozen foods.

Keywords: Packaging technology, Packaging material, Quality, Freezing, Frozen food

1. Introduction

Freezing is a promising technology to preserve quality and prolong shelf-life of food and agriculture products. Several factors impact quality of frozen foods including freezing process, food components, packaging, storage and distribution chain, and thawing. The freezing process governs the ice formation and initially changes microstructure of frozen products. The rate of heat removal during freezing determines the size and distribution of ice crystal formed which directly impact quality of frozen foods. Faster freezing leads to formation of small size of ice crystals. In general, food structures may be damaged by ice formation giving textural changes upon thawing and, therefore, small ice crystals are desirable to preserve frozen food quality.

The principle of food preservation by freezing include (i) the reduced temperature and thus decreased several chemical and biochemical reactions including microbial growth and respiration of fresh produce, and (ii) the reduced amount of water due to water transformation into ice conforms to the principle of food preservation as reduced water activity (a_w) and reduced molecular mobility [1, 2]. However, migration of water and gas diffusion possibly occurs at freezing temperature which subsequently cause deterioration of frozen foods e.g. ice recrystallization, dehydration and lipid oxidation which are accelerated by temperature fluctuation during cold chain. Moreover, the thawing increases water availability for microbial and

chemical reactions and thus accelerate loss of quality and safety of frozen products.

Packaging plays an important role on quality preservation of food products. The basic functions of packaging include (i) protection and preservation, (ii) containment, (iii) provide convenience, and (iv) giving information and communication [3]. The packaging materials provides barrier against environmental accelerated quality changes including gas and water vapor transmission. Several packaging technologies including modified atmosphere packaging (MAP), edible film/edible coating, active and intelligent packaging have been investigated and show effectiveness on enhancing quality of various food products.

This paper reviews the utilization and properties of packaging materials and technologies applied in frozen foods and their effectiveness on frozen food quality. Moreover, the principle of phase transition during freezing and quality deteriorations of frozen foods are demonstrated.

2. Freezing and phase transitions

Freezing process causes phase transitions of water and, in some cases, solute components. The cooling/freezing involves the removal of sensible heat and latent heat which associated with the reducing temperature and phase changes, respectively. The mechanism of ice crystallization consists of 2 processes namely nucleation and growth. A nucleus or seed with a critical radius is required before the ice can form and the process to produce such seed is called 'nucleation' [2, 4]. Consequently, the addition of water molecules to the solid-liquid interphase or 'growth' can occur once the stable nucleus is formed. The growth may not be instantaneous because the phase change

conforms to the release of heat and the ability of water to diffuse towards surface. The latent heat associated with phase change is much larger than that of sensible heat and is need to be removed so that the ice can form. Moreover, solutes must also be rejected from the growing ice surface as ice tends to form pure crystals [2]. Accordingly, the heat and mass transfer control the growth of ice crystals.

The time-temperature record during freezing process or so called 'freezing curve'; 'freezing profile' are shown in Figure.1a and 1b for pure water and food system, respectively. The removal of sensible heat ($4.18 \text{ kJ kg}^{-1}\text{°C}$) reduces temperature of the systems from initial temperature (point A) to that can fall below 0°C without the formation of ice crystals because nucleation is required for the crystallization. Once the critical mass of nuclei is reached, the system nucleates (point B) and releases its latent heat (335 kJ kg^{-1} at 0°C) showing the abrupt increase in temperature (point B to C) which represents the onset of ice crystallization. The lowering of temperature below the freezing point of materials without solidification is called supercooling. The supercooling is generally lower in aqueous solutions than in pure water because the presence of solute promotes heterogeneous nucleation which accelerates the nucleation [4]. When crystallization begins, the temperature reaches point C, the freezing point, which is 0°C for pure water and below 0°C for solution and food systems. The further cooling causes ice formation and reduced amount of liquid water. In pure water system, the liquid-solid transition of water takes place at an identical temperature. Conversely, the increased concentration of unfrozen phase causes instant decreased freezing point due to colligative effect as

water forms ice. The freezing point depression is determined by the number of dissolved solute molecules [4]. Upon solidification, further removal of heat decreases temperature of the systems toward freezer temperature (point E in pure water system). The decreased temperature possibly causes solute crystallization at point D in Fig.1b, and

the crystallization of solute releases latent heat of fusion that raises the temperature to eutectic equilibrium point that remains constant during eutectic solidification (point E to point F). Subsequently, the further cooling to freezer temperature (point G) is achieved after the solidification is completed.

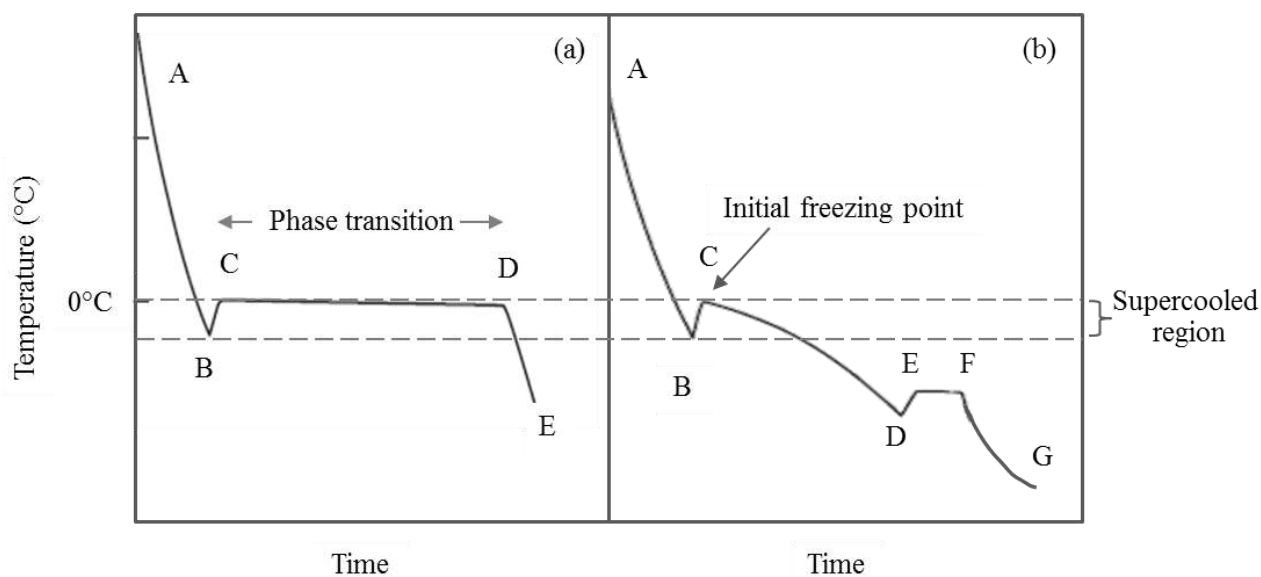


Figure 1 Typical time-temperature record (freezing curve) of frozen (a) pure water and (b) food systems.

As the phase transition of water is achieved, the system composes of ice and unfrozen phase or so called 'freeze-concentrated unfrozen solutes/matrix'. As the water transforms into ice, the concentration of unfrozen phase increased which substantially increases viscosity of the unfrozen matrix. When the viscosity reaches 10^{10} - 10^{12} Pa s, solidification without crystallization (vitrification) occurs, and the freeze-concentrated unfrozen phase becomes a glass which is an amorphous meta-stable state of materials [5, 6]. The temperature at which the transition takes place is called glass transition temperature which occurs in a range of temperature. If the cooling rate is slow

enough, the maximum ice formation can be achieved at a certain temperature called T_m' , below which the unfrozen systems progress no further ice formation. The further decreased temperature reaches the glass transition temperature of the maximally-freeze-concentrated systems or T_g' . The molecular mobility of the systems is restricted in the glassy state and the reaction kinetics and molecular mobility depend on the different between storage and glass transition temperature or $T-T_g'$ [7]. The physical state of unfrozen matrix affects the stability of frozen foods as most chemical reactions relate to the molecular diffusion of reactants. Accordingly, the storage temperature is a direct factor affecting

frozen food quality and shelf-life e.g. a product retains its good quality for months at -20°C but can deteriorate in a few days at -10°C . However, the frozen storage at -18°C corresponds to an optimum between the financial costs and the shelf life of frozen products [6]. Unfortunately, the T_g^1 of frozen foods and desserts are well below -18°C and, therefore, diffusion of reactants still take place leading to several quality deteriorations.

3. Quality deteriorations of frozen foods

The major quality loss of frozen products attribute to physical and chemical deteriorations. The migration of water is a major physical changes; whereas, chemical changes of frozen foods include lipid hydrolysis and oxidation, protein denaturation and oxidation, enzymatic activity, degradation of vitamin and color pigment, and flavor changes [4, 6].

Water migration with and without change in water content is the major physical deterioration of frozen foods. The ice recrystallization causes no changes in water contents, however, impacts the texture of frozen products e.g. sandy texture in ice cream and frozen desserts, increased enzymatic reactions and drip loss upon thawing of fresh produce and meat products due to cell wall and tissue damage. The water migration with the change in water content includes water loss and water translocation within products with heterogeneous water content e.g. pastry and filling. The ice sublimation causes loss of water from frozen food which affects organoleptic properties including appearance of both frozen food and package as well as reduced weight of frozen products. The dehydration occurs, particularly, at the surface contributes to the glassy appearance due to the presence of tiny cavities known as 'freezer burn' [8].

Moisture in frozen foods tends to diffuse from the center to surface and sublimated into the headspace between product and package. The different in chemical potential and activity of water promotes water migration. The water vapor pressures in the frozen systems are determined by the temperature and independent of components. Accordingly, the temperature gradient due to temperature fluctuation within package causes the vapor flux and thus accelerates water migration. The decreased temperature leads to the decreased water vapor pressure; therefore, the vapor tends to crystallized at a colder surface of food and packaging due to a less vapor pressure known as 'frost' formation which obviously affects consumer's appeal [9]. The elimination of package effectively prevents frost formation due to the absence of headspace.

Lipid oxidation cannot be inhibited at freezing temperature and occurs by both enzymatic and non-enzymatic reactions. Moreover, the dehydration of surface due to ice sublimation increased O_2 exposure which enhances oxidation and consequently produces rancidity off-flavor. The extent of lipid oxidation is influence by the amount and degree of saturation of lipids i.e. highly unsaturated lipids are prone to oxidation than saturated ones. Polyunsaturated fatty acids are autoxidized in the presence of oxygen forming hydroperoxides which subsequently decompose into volatile compounds, forming off-flavor and off-aroma compounds [6]. Moreover, free radicals produced by autoxidation of lipids also initiate degradation of pigment and oxidation of protein components producing protein radicals that interact with other proteins or lipids forming protein-protein or protein-lipid aggregates [10]. Although oxidation

occurs slowly at freezer temperatures due to low temperature effect on rate of reaction, it remains a problem, since shelf-life of frozen foods is approximated as 6-12 months [6, 9].

Protein denaturation occurs in the unfrozen phase due to the change of environment namely the increased concentration of salts in the unfrozen phase by; the high ionic strength that produce competition with existing electrostatic bonds and thus modify the native protein structure [4]. The denaturation of proteins causes a consequent decreased solubility, altered water binding capacity, loss of biological activity, particularly enzymatic, and increased susceptibility to attack by proteases due to the unmasking of peptide bonds in unfolded structures [6]. Protein aggregation may subsequently occur due to decrease in protein-water hydrogen bonding and an increase in protein-protein interactions.

Enzymatic activity including hydrolytic enzymes (hydrolases such as lipases, phospholipases, proteases, etc.) can remain active during frozen storage. The hydrolysis of lipids can lead to undesirable flavor and textural changes; whereas, proteases catalyze the hydrolysis of proteins to peptides and amino acids. Moreover, the browning of plant tissue is caused by enzymatic oxidation of phenolic compounds in the presence of oxygen [4]. The ice formation causes cellular damage which enhances the exposure between enzymes and substrates that catalyze reaction. Blanching effectively inactivate enzymes and is typically applied before freezing of various vegetables.

Flavor loss and odor pick up affect consumer acceptability leading to quality loss of frozen foods. Deterioration of flavor involves

rancidity, bitterness or undesirable fishy taste, owing to the formation of low-molecular-weight compounds from lipid oxidation, protein denaturation and enzymatic activity. Accordingly, several reactions such as moisture migration induced cell damage, lipid oxidation due to enzyme and non-enzymatic reactions, and protein denaturation promote off-flavor formation [10].

4. Packaging materials

Suitable packaging provides an effective barrier to the loss of moisture and flavor/volatiles from the food to the external environment as well as the exposure to oxygen and thus plays a key role to minimize quality loss of food during frozen storage and distribution. The essential requirement of packaging materials include temperature stability, barrier properties, insulation properties, compatibility with packaging machinery and packaging systems, and consumer appeal [11]. Physical and chemical stability of packaging materials over a broad range of temperature, i.e. below the freezer temperatures and high temperatures during the cooking of the food package in the microwave or conventional oven of 'ready-to-eat' or 'ready-to-cook' frozen products, are important. Moreover, thermal insulation and heat-transfer resistance materials help maintain low temperatures for frozen foods during cold chain distribution, e.g. thicker package wall, multilayered wall structure, impervious sealing and foamed material (such as polystyrene foam) and air space for insulation function, and helps minimize temperature fluctuations that accelerates degradation of the products [9, 12]. Several packaging materials i.e. plastics, paper and paperboard, and aluminium are used to pack frozen foods.

4.1 Plastic

Plastic packaging is typically produced by synthetic polymers with some additives such as plasticizer, anti-fogging etc. Synthetic plastics have wide range of physical, mechanical and barrier properties depending on their structures. Numerous plastic packagings were used for frozen foods including polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyvinylidene chloride (PVDC), polystyrene (PS), polyethylene terephthalate (PET), ethylenevinyl acetate (EVA) and polyamide (nylon). Several properties and structures of some plastic materials are shown in Table 1

PE materials have good mechanical and easy processing properties that can be used with 'form-fill-seal' packaging systems. PE bags are commonly used to pack individual quick frozen foods (IQF) e.g. fruits, vegetable and shellfish [11, 14]. The materials have a good heat sealing property with low cost and therefore, can be used as a layer for heat-sealing. PE can also be classified into high density (HDPE) and low density (LDPE) due to the different side chain branching and crystallinity which directly affect their physical, mechanical and barrier properties. HDPE has relatively few side chains and can withstand high temperature in excess of 100°C as for 'boil-in-bag' packaging; whereas, LDPE is stretchiness, clarity, heat sealability and low cost [9, 11].

PP has the lowest density among major plastic materials but high tensile strength, hardness and stiffness; however, it cannot tolerate freezing temperature and shows cracking which limited its effectiveness as a single material for packaging of frozen foods.

PVC is a naturally hard and brittle material that is usually modified with plasticizers to improve

its mechanical properties; however, it has high oil resistance, barrier properties and better clarity than HDPE. PVDC films are clear, soft, good oxygen barrier and excellent cling characteristics and, therefore, can be used for vacuum skin-tight of frozen poultry [9, 14].

PS is a clear, hard, brittle and low-strength material with a melting point around 90°C and poor impact strength but high resistance to freezer temperature. The modification with elastomer e.g. butadiene produce high-impact polystyrene (HIPS) which is more suitable for freezer temperature. HIPS is widely used for deep-draw packaging e.g. egg trays, ice cream containers and cups. Addition of foaming agents produce expanded polystyrene (EPS) that is a poor heat conductor and hence an insulation against high and low temperatures for frozen foods [9, 11, 14].

PET is a major plastic used for food packaging that need to be biaxially-oriented to improve its clarity and mechanical properties. It can tolerate very high and low temperature and acts as a better O₂ barrier than PE and PP. The crystallized PET is able to withstand up to 220°C and hence frequently used for frozen ready meals that is precooked in microwave and conventional dual oven [9].

Nylon 6 is a common polyamide used for food packaging. It produces clear film which acts as a gas and aroma barrier but poor moisture resistance, however, a superior strength and puncture resistance at low temperature [14].

4.2 Paper and paperboard

Paper and paperboard are commonly used as individual package and secondary package that contain several boxes containing individual package.

Although the barrier properties against O₂ and other gases of paper-based materials are poor, they provide structural support that protects frozen foods from mechanical damage and is also used to separate heterogeneous food components [9]. Paper packaging is commonly laminated with other materials i.e. wax, plastic and aluminium to achieve

desirable barrier and printing quality such as PET-laminated paper is used as dual ovenable trays, PE-laminated for heat sealing properties. The heat transfer resistance of paperboard may be a problem during freezing process; however, it may minimize effects of temperature fluctuation during frozen storage that leads to quality loss.

Table 1 Structure and properties of plastic materials for packaging of frozen foods

Material	Structure	Density (kg/m ³)	Tensile strength (GPa)	Elongation (%)	T _m (°C)	T _g (°C)	WVTR (g/m ² day)	OTR (mL/(m ² day))
PE								
LDPE	$\left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{---C---C---} \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_n$	910-925	0.01-0.03	200-600	115	-110	16-31	7750
HDPE	$\left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{---C---C---} \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_n$	945-967	0.02-0.04	200-600	137	-90	6	1550-3100
PP	$\left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{---C---C---} \\ \quad \\ \text{H} \quad \text{CH}_3 \end{array} \right]_n$	900	0.14-0.20	50-275	176	-18	6	1550-2480
PVC	$\left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{---C---C---} \\ \quad \\ \text{H} \quad \text{Cl} \end{array} \right]_n$	1220-1360	0.03-0.06	100-400	212	87	31-465	465-9300
PVDC	$\left[\begin{array}{c} \text{H} \quad \text{Cl} \\ \quad \\ \text{---C---C---} \\ \quad \\ \text{H} \quad \text{Cl} \end{array} \right]_n$	1600-1700	0.06-0.11	50-100	202	-17	0.8-5	0.8-5
PS	$\left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{---C---C---} \\ \quad \\ \text{H} \quad \text{C}_6\text{H}_5 \end{array} \right]_n$	1050	0.06-0.08	2-30	240	100	109-155	3100-5430
PET	$\left[\begin{array}{c} \text{H} \quad \text{H} \quad \text{O} \quad \text{O} \\ \quad \quad \quad \\ \text{---O---C---C---O---C---C---} \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_n$	1400	0.17-0.23	70-130	265	69	16-23	50-90
EVA	$\left[\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ \text{---C---C---C---C---} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{O} \quad \text{COCH}_3 \end{array} \right]_n$	930	0.01-0.02	500-800	90	-33	31-47	10,850-13,950
Nylon 6	$\left[\begin{array}{c} \text{O} \quad \text{H} \\ \quad \\ \text{---C---C---C---C---} \\ \quad \\ \text{H} \quad \text{N} \end{array} \right]_n$	1140	0.17-0.26	70-120	220	47	155	15-30

T_m = Melting temperature, T_g = Glass transition temperature, WVTR = Water vapor transmission rate, OTR Oxygen transmission rate
Source: Yam et al., 2004; Agroui et al. (2012); Lee & Sun (2012); Butler & Morris (2013); Robertson, 2013

4.3 Aluminium

Aluminium is a light metal and has low density that is harmless to health and even has antibacterial effect [16]. It resists to corrosion and

prevents penetration of gas, water vapor, foreign substances, and light thus giving a high protection for frozen foods. Aluminium has high thermal stability over the wide range of temperature from -70°C up

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to 600°C. The high electric and thermal conductivity of aluminium support its utilization for oven baking dish and giving browning and crispiness for ready-meals. Moreover, the metallic sheen characteristic of metal acts as self-promoting packaging that appeals consumer of high quality products [16].

It is obviously that no single packaging material may offers all the desirable features e.g. temperature tolerance, barrier properties, printing and sealing properties; therefore, combination of the desirable characteristics of individual materials may provide an excellent suitable packaging. Lamination and co-extrusion are used to develop and produce desirable characteristic packaging such as biaxially oriented polypropylene (BOPP), BOPP coated by acrylic copolymer, metallized BOPP by aluminum, and LDPE [17]; laminated PE/aluminum/PET film, and a co-extruded polyolefin film [18].

5. Packaging technologies

5.1 Modified atmosphere packaging

Typical gaseous composition of dry air at sea level are nitrogen (N₂) 78.03%, oxygen (O₂) 20.99%, argon (Ar) 0.94%, carbon dioxide (CO₂) 0.03%, hydrogen (H₂) 0.01%. The modification or alteration of gaseous and atmosphere surrounded foods is known as modified atmosphere packaging (MAP) which includes the vacuum packaging (VP) i.e. the air is removed in the presence or absence of headspace. The MAP technology has been applied to prolong shelf-life of fresh and low temperature storage of food and agriculture products. The permeation of packaging material is a critical factor controlling the effectiveness of MAP. The major gas used in MAP includes O₂, N₂ and CO₂.

O₂ has major role in cellular respiration and retaining a desirable cherry-red color or 'bloom' of

red meat due to the presence of oxymyoglobin. However, high O₂ possibly promotes oxidative degradation of lipid, protein, pigments, vitamin, etc. leading to quality loss of foods as discussed in section 3. CO₂ functions as bacteriostatic and fungistatic in MAP [3]. The high solubility of CO₂ in food components can cause 'package collapse' unappealing to consumer that can be prevented by addition of N₂ to remain package volume. N₂ is an inert gas that has no relevance to chemical and biochemical reaction and thus is used in MAP to replace O₂ preventing oxidative reaction.

The dehydration and subsequent frost formation is a major deterioration of frozen foods that is obviously detected by the consumer due to the precipitation of the water vapor within the headspace onto surface of foods and/or package. Therefore, the vacuum skin-tight packaging systems which eliminate headspace within package effectively inhibit ice sublimation and subsequent water loss, freezer burn and frost formation of frozen foods. The VP system is successful to pack several frozen products including seafood, meat and poultry; however, the color loss of red meat due to reduced oxymyoglobin is primary concern since color is a major factor affecting consumer choice for buying red meat products [19]. The MAP systems also affect lipid oxidation, color, firmness and sensory qualities of frozen foods as shown in Table 2.

5.2 Edible films and coatings

Edible film and coating refer to a thin layer of edible materials that cover foods to improve overall quality and extend shelf life of food products by increased functional barriers to moisture, gas, and solute transmission [8]. Edible film is a preformed and stand-alone solid sheet that is then used to wrap

products; whereas, a coating is applied in liquid form such as dipping or spraying and formed sheet directly on food surface itself [25, 26]. The edible films and coatings reduce the rate of moisture transfer between the food and the surrounding atmosphere, thus decreased freezer burn and also eliminate quality changes associated with the oxidation of lipids, vitamins, pigments, and flavor compounds via their good oxygen-barrier properties [8]. The edible film-forming materials are polysaccharide, protein, lipids and multi-components. Several edible materials applied as edible films and coatings of frozen foods and their benefits are shown in Table 3.

Polysaccharides are water-soluble which dissolve in and form intensive hydrogen bonds with water contribute to thickening and/or gelling of the aqueous solutions. The film characteristic influenced by the extent of intermolecular hydrogen bonding between polymer chains due to molecular structures including the presence or absence of branching, electrical charge, substitution of sugar units, and molecular weight [40]. The polysaccharide-based film-forming materials e.g. starch, modified starch, cellulose derivatives namely carboxymethyl cellulose, methyl cellulose, hydroxypropyl cellulose and hydroxypropyl cellulose, alginate, carrageenan, pectin, pullulan, chitosan, gellan gum, xanthan gum and agar contain large number of hydroxyl group contributes to hydrophilic property. Polysaccharide-based films and coatings provide a good barrier to O₂ and CO₂ under certain conditions (temperature and relative humidity), but a poor barrier to water vapor due to their hydrophilic nature [8].

Protein film-forming materials come from plant, meat, egg and milk including collagen, gelatin,

casein, whey protein, corn zein, wheat, gluten, soy protein, egg white protein, fish myofibrillar protein, sorghum protein, pea protein, rice bran protein, cottonseed protein, peanut protein and keratin [41]. Proteins are good film formers exhibiting excellent O₂, CO₂, and lipid barrier properties, particularly at low relative humidities. The denaturation or modification of secondary, tertiary, and quaternary structures of proteins controls desirable film physical, mechanical and barrier properties such as heat denaturation, pressure, irradiation, mechanical treatment, acids, alkalis, metal ions, salts, chemical hydrolysis, enzymatic treatment, and chemical crosslinking [41, 42].

Lipids and resins including waxes e.g. beeswax, paraffin, carnauba wax, candelilla wax, rice bran wax, resins e.g. shellac, terpene, and acetoglycerides are film-forming materials which have poor mechanical properties and are mostly soft solids at room temperature. Heat treatment causes reversible phase transitions between fluid, soft-solid, and crystalline-solid states that used to mold and casting lipid materials [41]. Edible films and coatings made from lipid materials have very high water resistance and low surface energy due to their hydrophobic nature with a glossy surface such as those found in candy and chocolate products. Accordingly, the lipid-based substances are incorporated into polysaccharide and protein polymeric matrix to improve the moisture barrier of the films and coatings. Several factors affect water barrier properties lipid-based films and coatings namely number of carbon atom, degree of saturation, lipid polymorphism and homogeneity of distribution [8].

Table 2 Effects of modified atmosphere packaging (MAP) on frozen food quality

Food	MAP conditions	Storage	Packaging materials	Quality	Sensory	Reference
Boiled shrimp	100%N ₂	-17 °C	3-layer laminated (Oriented PA/cast PA/low linear density PE)	Oxidation: MAP inhibited TBARS increased up to 9 months. TBARS value of MAP was 25% of non-MAP systems at 12 month of storage indicated reduced oxidation. Astaxanthin (red color): MAP slowed and decreased amount of astaxanthin loss in frozen shrimp. Frost: Temperature fluctuation accelerated frost formation which cannot be inhibited by MAP.	Rancid flavor: MAP inhibited rancidity flavor formation up to 9-12 months. Toughness: MAP reduced toughness increase up to 6-9 months. Color: MAP decreased color fading and retained color score after 3 months; whereas, non-MAP decreased continually.	[20]
Turkey meat	VP 60%CO ₂ + 40%N ₂	-20 °C	14-layer laminated PP/PA/PE film 7-layer laminated PA/PE film	Oxidation: VP and gas-MAP reduced TBARS and hexanal increase up to 6 months; whereas non-MAP increased sharply after 3 months. Insignificant difference was observed between VP and gas-MAP.	-	[21]
Lasagne (beef+ pasta+ cheese+ sauce)	40%CO ₂ + 60%N ₂ 40%CO ₂ + 30%N ₂ + 30%O ₂	-25 °C	N/A	Color: CO ₂ /N ₂ /O ₂ system was less bright than CO ₂ /N ₂ and non-MAP (air) for non-reheated systems; however, the atmosphere had no effect on lasagna color after heating. Firmness: CO ₂ /N ₂ samples were firmer (higher shear force) than air systems of reheated lasagna. Total viable count: CO ₂ /N ₂ /O ₂ > CO ₂ /N ₂ > air in unheated systems. Drip: MAP had no effect on drip loss.	-	[22]
Coho salmon	VP VP + polyphenol coated PE film	-18 °C	PE PE coated with <i>p</i> -coumaric and ferulic acid	Lipid oxidation: VP inhibited peroxide and conjugated diene formation, reduced anisidine values. Lipid hydrolysis: VP and polyphenol cannot prevent free fatty acid formation in frozen salmon due to lipase and phospholipase activities. Tocopherol: VP reduced loss of α - and γ -tocopherol. Polyphenol had extra benefit to maintain α -tocopherol.	Rancid odor: VP inhibited increase of rancid odor during frozen storage. A difference was found between VP and non-VP (air) package during 15-18 months. Polyphenol had no additional effect on rancid odor development.	[23]
Sugar-apple	VP	IQF (-48°C) and frozen storage	PVDC/nylon bags	Color: VP retained lightness and greenness of pericarp (L, a, b, Hue) PPO activity: VP had higher PPO activity than non-VP (air). Phenolic compounds: Gallic acid, eugenol, catechin and chlorogenic acid was lower in non-VP than VP due to conversion to browning products by PPO and other oxidation-related enzymes. Chlorophyll: VP decreased chlorophyll degradation.	-	[24]

Table 3 Biomaterials used for edible films and coating and their functions in frozen foods

Materials	Film/ coating	Frozen Food	Functions	References
Polysaccharide				
Pectin	coating	pre-fried cassava product	Moisture retention during deep-frying (depend on products) Decreased fat adsorption during frying	[27]
Cellulose derivatives				
Methyl cellulose	film	sundae ice cream cone	Retard moisture transfer from ice cream to sugar cones	[28]
Methyl cellulose-palmitic acid			Additional moisture barrier with palmitic acid	
Methylcellulose	coating	cowpea paste	reduced oil uptake during deep-frying	[29]
Hydroxyl methyl cellulose	coating	cowpea paste	reduced oil uptake during deep-frying	[29]
Cellulose ether-beeswax coated	film	bread-pizza sauce	Retard moisture transfer from sauce to bread	[30]
Chitosan	coating	Pink salmon	Reduced moisture loss during frozen storage	[31]
		silver carp	Delayed lipid oxidation Inhibited lipid oxidation	[32]
		lingcod	Delayed increase of total volatile basic nitrogen Inhibited ATP degradation	[33]
		strawberries	Reduced drip loss Decreased lipid oxidation Reduced total plate and psychrotrophic counts	[34]
			Reduced drip loss Maintain texture properties (peak force) because less moisture migration and thus high integrity	
Sodium-alginate	coating	pork	decreased thawing loss	[35]
Amylose	coating	cowpea paste	reduced oil uptake during deep-frying	[29]
Protein				
Whey protein	coating	pre-fried cassava product	Moisture retention during deep-frying (depend on products) Decreased fat adsorption during frying	[27]
Whey protein concentrate	coating (after freezing)	Atlantic salmon	Delayed lipid oxidation Increase thaw yield Decreased drip loss	[36]
	coating	Atlantic salmon	Reduced weight loss during cooking Delay lipid oxidation	[37]
Whey protein isolate	coating	Atlantic salmon	Reduced weight loss during cooking Delay lipid oxidation	[36]
Whey protein isolate + acetylated monoglyceride	coating (bilayer)	King salmon	Reduced rate and amounts of moisture loss Delayed lipid oxidation, reduced peak peroxide values	[38]

Table 3 (continued)

Materials	Film/ coating	Frozen Food	Functions	References
Soy protein concentrate	coating	Pink salmon	Reduced moisture loss during frozen storage Delayed lipid oxidation	[31]
Soy protein isolate	coating	pre-fried cassava product	Moisture retention during deep-frying (depend on products) Decreased fat adsorption during frying	[27]
Egg albumin	coating	Pink salmon	Reduced moisture loss during frozen storage	[31]
Corn zein	coating	cowpea paste	reduced oil uptake during deep-frying	[29]
Whole egg + bread crumb powder	coating	buffalo meat	Decreased lipid oxidation Decreased tyrosine value due to minimal protein degradation	[39]
Lipid				
Acetylated monoglyceride	coating	King salmon	Reduced rate and amounts of moisture loss Delay lipid oxidation, reduced peak peroxide values	[38]

5.3 Active Packaging

The traditional packaging must be inert which provide passive protection against environmental conditions or influences that affect shelf-life of food products; however, active packaging is design to interact with the contents and/or the surrounding environment to increase shelf-life and some quality parameters of foods [43]. European FAIR-project CY 98-4170 defined active packaging as the packaging that changes the condition of the packaging to extend shelf-life or improve safety or sensory properties while maintaining the quality of the foods [44]. The active function can be delivered as (i) the independent systems e.g. bags, strips or labels which are incorporated into or attached to the inside of package as separate items or (ii) the integrated systems into the packaging material itself and not visually perceptible as distinct elements [43]. Several developed active packaging systems and

mechanism are shown in Table 4 namely O₂ scavengers, ethylene scavengers, CO₂ scavengers and emitters, moisture absorbers, ethanol emitters, flavor absorbing/releasing, anti-fogging and anti-sticking, light absorbers, microwave susceptors, antioxidant packaging [44, 45].

Oxygen scavenger eliminates O₂ within the packaging by incorporated substances based on chemical and enzymatic oxidative reactions e.g. iron, organic substances and anthraquinone dye. The oxidation of such compounds is activated by some catalyst e.g. moisture, light and metals [12]. The MAP or VP technologies cannot completely remove O₂ and the permeability of packaging materials may contribute to the presence of oxygen within package that causes oxidative deterioration of frozen products. The addition of oxygen scavenging systems in the forms of sachet, dispersed/embedded, layered package effectively remove residual oxygen in the package [45]. However, the

speed and capacity of oxygen scavenging system in frozen food may be different from those at ambient or chilled storage conditions because the low temperature affects the rate of oxidation [12].

Water loss due to ice sublimation causes surface desiccation that accelerates quality deterioration. The addition of sachets containing hygroscopic sugar and inorganic salt to maintain high relative humidity inside the package possibly reduces the water loss from frozen products [12]. As the water activity of the frozen systems is governed by the temperature, the gradient of storage temperature contributes to water migration due to a non-uniform vapor pressure [9]. Temperature fluctuation of frozen foods may lead to partial ice melting; however, a sachet of moisture absorber/desiccant is not typically incorporated into the packaging of frozen foods because it may cause a gradient of water activity that adversely affects quality of frozen products [12]. The melted liquid water can cause deterioration by chemical and microbial reaction, therefore, a simply moisture absorbent pad may be placed to eliminate drip during thawing.

Antioxidant incorporated packaging has been widely applied in various foods in both synthetic and edible packaging. Some applications of antioxidant packaging in frozen foods are shown in Table 5. Oxidative reaction produces free radicals which are highly active. Several natural and synthetic antioxidant compounds efficiently react with free radicals forming a non-reactive substance and inhibit further oxidation. Antioxidants act as radical scavengers that effectively eliminate free radicals as soon as they are formed and, therefore, neither high-barrier nor vacuum packaging materials would be required to avoid oxidation [43]. The

maximum efficiency of antioxidant packaging can be achieved by the control-release systems of antioxidant compounds to balance with lipid oxidation over storage time. Several factors such that antioxidant diffusivity, loading, and package layer thickness are important variables to improve antioxidant active function [50].

Antimicrobial packaging can inactivate microorganisms those present on food surface. The typical freezer temperature inhibits microbial growth (<-10°C), however, cannot inactivate them. The microbial activity is recovered upon thawing due to the raised of temperature and water activity suitable for microbial growth which accelerates loss of quality and safety of frozen foods. As previously mentioned, aluminium packaging also have toxic effects to microorganisms due to the modification of ion transport, and binding to ATP, DNA, membranes, enzyme or cell walls of microbes [51]. The typical antimicrobials incorporated in food packaging are organic acids, chitosan, nisin, lactoperoxidase, and some plant extracts and their essential oils which must be selected by the effectiveness against the target microorganism. The interactions among the antimicrobial, the film-forming biopolymer, and other food components can modify the antimicrobial activity and the characteristics of the film [52]. The antimicrobial packaging can be in the forms of [48, 53]:

1. Sachets or pads containing volatile antimicrobial agents that give benefit for foods with irregular shape as volatile can diffuse freely through uneven surface.

2. Dispersion/Incorporation/Immobilization of volatile and non-volatile antimicrobial agents directly into polymers by extrusion, heat-press and casting.

3. Coating or adsorbing antimicrobials on polymer surfaces which are in direct contact with the food surface.

4. Polymer materials those are inherently antimicrobial e.g. chitosan, UV-irradiated nylon, polymers containing quaternary ammonium [12].

Flavor release and absorber can eliminate and/or mask the undesirable flavor, such as rancidity from oxidation and breakdown of proteins in fish muscle, and thus improve quality of frozen foods. Packaging materials, particularly plastic, can interact with flavor compounds and cause flavor loss due to molecular adsorption known as 'scalping' [45]. Therefore, the control-releases of flavor and aroma during thawing and/or microwave heating and cooking would improve organoleptic and consumer acceptance. However, the ethical issue should be considered that the active packaging should not mask the undesirable organoleptic properties due to quality loss, defects and/or spoilage of food products.

5.4 Intelligent Packaging

Intelligent packaging has the ability to track or monitor the product, environment inside or outside the package, and communicate that information with human [61]. An extensive review of intelligent packaging in food systems was demonstrated by Suppakul [62]. Some examples of intelligent packaging for foods are evidence of tampering, containment of a package breach, package integrity, quality and safety indicators, time-temperature indicators (TTIs), microbial growth, gas-sensing devices, pathogen detection, traceability/anti-theft devices, radiofrequency identification (RFID) labels, tags, chips, product authenticity which

can be categorized into 2 basic types [49, 61] namely:

- (i) Data carrier devices e.g. barcode labels and RFID tags that are used to store and transmit data, and
- (ii) Package sensors and indicators e.g. TTIs, integrity or gas indicators, freshness indicators (microbial or pathogen spoilage), gas sensors, biosensors, fluorescence-based oxygen sensors that are used to monitor the external environment.

The temperature indicators had been applied to monitor the handling of refrigerated and frozen food products along cold chain distribution (e.g. storage warehouses, transportation vehicles and retail outlets) in the United States. Such indicators can be classified into 3 categories [63, 64]:

1. Critical temperature indicators (CTI) which shows the exposure above (or below) a reference temperature but do not reveal if the temperature was lowered at a later time nor cannot show the history of exposure above the critical temperature. They show that the products experience an undesirable temperature for a sufficient time to cause a change critical to safety or quality of products such as the irreversible texture deterioration that occur due to phase change i.e. defrosting of frozen products [64].

2. Critical temperature/time integrators (CTTI) that reflect the combination of time and temperature that exposed above a critical temperature.

3. Time temperature integrators or indicators (TTI) which continuously reveal the combination of time and temperature dependent response throughout the product's history.

The devices are typically attached on packaging to provide visual indications of temperature history during distribution and storage, which warn the manufacturer and consumer of the temperature abuse for chilled and frozen products [61]. Systematic investigation of TTIs in quality control of frozen foods can be found by Singh &

Wells [65] and Giannakourou & Taoukis [66, 67]. The mechanisms of TTIs can be categorized as mechanical-, diffusion-, microbial-, enzymatic-, polymer-, and electrochemical-based [49, 67]. Several TTIs work based on color changes and color development which is correlated to quality loss of food products.

Table 4 Functions and mechanisms of active packaging in foods [12, 45-49]

Active function	Mechanisms/Compounds	Foods
O ₂ scavengers	Enzymatic reactions: Glucose oxidase-glucose → glucono-δ-lactone + H ₂ O ₂ Ethanol oxidase-ethanol → acetaldehyde Chemical reactions: Oxidation of ferrous (Fe ²⁺), nanocrystalline TiO ₂ Oxidation of ascorbic acid, unsaturated fatty acids and hydrocarbons Oxidation of photosensitive dye + singlet-oxygen acceptor to form bound oxygen (need light as oxidation catalyst) e.g. anthraquinone dye Oxidation of sulfites: 2SO ₂ + O ₂ + 2H ₂ O → 2H ₂ SO ₄ Palladium/alumina catalyst :oxidation of hydrogen to water Yeast or aerobic bacterial spore: respiration consume O ₂ and produce alcohol	Ground coffee, tea, roasted nuts, potato chips, chocolate, powdered milk, drinks, bread, pizza, refrigerated fresh pasta, fruit tortes, cakes, cookies, beer, meats, smoke and cured meats, fish, cheese
Ethylene scavengers	Activated carbon (charcoal)/ activated charcoal-bromine, activated carbon-palladium catalyst Activated earth and finely dispersed clays e.g. bentonite, Kieselguhr, zeolites, Japanese oya and other powdered mineral KMnO ₄ , KMnO ₄ -silica gel	Fruits e.g. kiwifruit, banana, avocados, persimmons
CO ₂ scavengers	Iron oxide, calcium oxide or lime	Roasted coffee
CO ₂ emitters	Sodium bicarbonate-citric-water	Meat, fish, fresh produce
Moisture absorbers	Desiccants e.g. silicates (i.e., silica gel), zeolites and humidity-controlling salt Cellulose fiber pads	Dried fruits and meat products, fresh meats
Ethanol emitters	Absorption or encapsulation of ethanol in a carrier material	Bakery products, fish
Flavor absorbing/releasing	Flavor/odor absorber e.g. activated clay, alumina, silica gel, odor-absorbing polymers or activated carbon. Acidic compounds such as citric in films can interact with amines formed by fish degradation. Flavor control-release by encapsulation or extrusion into packaging films	Fruit juice, ready meals, ground coffee, ice cream
Anti-fogging and anti-sticking	Biaxially oriented vinylon, compression rolled oriented HDPE	Fresh fruit and vegetable packages, soft candies, cheese slices
Light absorbers	UV blocking agents, hydroxybenzophenone	Frozen ready meal, pizza, milk
Microwave susceptors	Metallized thermoplastics	Ready-to-eat meals
Antioxidant packaging	Synthetic antioxidant: BHA, BHT, TBHQ and Irganox® Natural antioxidant: tocopherol, ascorbic acid, curcumin, tyrosine, essential oils and plant extracts of barley husks, borage, cinnamon, citronella, clove, ginger, green tea, marigold, murta leaves, rosemary, oregano, thyme, etc.	Cereals, meat, fish, frozen fruits

Table 4 (continued)

Active function	Mechanisms/Compounds	Foods
Antimicrobial packaging	<p>Metal and metal oxide materials: silver (Ag), gold (Au), zinc oxide (ZnO), silica (SiO₂), titanium dioxide (TiO₂), alumina (Al₂O₃), and iron oxides (Fe₃O₄, Fe₂O₃).</p> <p>Enzymes: lysozyme, lactoperoxidase, glucose oxidase, alcohol oxidase</p> <p>Bacteriocins (peptide or small proteins): nisin, lactocins, pediocin, diolococin, and propionins</p> <p>Plant extracts: polyphenolic compounds and phenolic acids. Polyphenols can penetrate the semipermeable bacterial membrane and react with cytoplasm or cellular proteins, destabilizing microbial cells.</p> <p>Essential oils: terpenes, terpenoids, and aromatic constituents e.g. garlic oil, cinnamon, clove, ginger, rosemary, oregano, dill, and basil extracts which are more active against Gram-positives than Gram-negatives. The antibacterial effect depends on the hydrophobic character of the oils that might separate the lipids of the bacterial cell membranes, making them more permeable. Essential oils can also inhibit the production of bacterial essential enzymes or affect bacterial genetic materials.</p> <p>Anhydrides and weak organic acids e.g. acetic, benzoic, lactic, citric, malic, tartaric, propionic, fumaric, or sorbic acid. Dissociated form of the acids freely diffuse across the microbial cell membrane resulting in cytoplasm acidification.</p> <p>Ethylenediaminetetraacetic acid (EDTA) by disrupting the lipopolysaccharide structure of Gram-negative bacteria by chelating Ca²⁺ and Mg²⁺ salts.</p> <p>Antimicrobial macromolecules e.g. chitosan which the positive charge of amino group at pH below 6.3 interacts with the negatively charged cell membranes. ϵ-Polylysine is a natural antimicrobial polypeptide with polycationic nature, that interact extensively with bacterial membranes.</p> <p>Radiation-emitting material films which emit long-wavelength infrared radiation on exposure to water or water vapor is effective against microorganisms.</p>	<p>Fruit juice, fresh meat, cured meat/ ham, fish fillets, sausages, seafood, cheese, fresh-cut fruits and vegetables, salad</p>
Self-heating/cooling	<p>Self-heating: Exothermic reaction of CaO hydration, reaction of acid-alkaline earth oxide (CaO, BaO), reaction of anhydrous CaCl₂ with water, reaction between KMnO₄ and glycerine, reaction between CuSO₄ and zinc, and oxidation of iron and magnesium by salt water</p> <p>Self-cooling: zeolite-technology</p> <p>Steam cooking: moisturized paper pad in microwavable package</p>	<p>Rice, Ready-to-eat meals</p>

Table 5 Applications of active compounds incorporated packaging materials for frozen foods

Active compounds	Active functions	Packaging matrix	Incorporation method	Food	Storage temperature /time	Quality parameters	Reference
BHT	antioxidant	LDPE films	blow-extrusion	Sierra fish fillets	-25°C 120 d	BHT-LDPE reduced lipid oxidation, thiobarbutyric acid, peroxide values and free fatty acids, decreased tissue damage, reduced loss of firmness and minimized protein damage and denaturation.	[54]
Barley husk extract	antioxidant	LDPE films	coating	salmon, halibut, hake, cod blue shark, swordfish	-20°C 12 mo	Natural extract from husk barley slowed down lipid hydrolysis and increased oxidative stability as determined from peroxide value, conjugated dienes, conjugated triene hydroperoxides, free fatty acids, totox value, thiobarbituric acid index and <i>p</i> -anisidine value.	[43, 55-58]
Oregano essential oil (OEO) Potassium sorbate (KS)	antioxidant antimicrobial	Starch-Ecoflex® films	blow-extrusion	chicken steak	frozen storage	OEO and KS decreased oxidation. Active compounds reduced microbial population (total viable count, total coliforms and <i>E. coli</i>) during frozen storage	[59]
Borage extract	antioxidant	gelatin film	solution mixing	horse mackerel patties	-20°C 240 d	TBARS and peroxide values were reduced indicating inhibited lipid oxidation. Phenolic compounds from the borage films diffused to the patties and increased the antioxidant capacity of the muscle as determined from ferric reducing capacity (FRAP).	[60]

6. Conclusion

Freezing prolong shelf-life of food and agriculture products; however, several quality deteriorations possibly take place which are accelerated by temperature fluctuations during frozen storage and cold chain distribution. The moisture loss from frozen foods accelerated quality deteriorations i.e. frost formation, dehydration, freezer burn, texture, lipid oxidation and off-flavor

formation. The appropriate selection of packaging materials (synthetic plastic, paper, aluminium, edible films) and packaging technologies can minimize the undesirable physical, chemical, biochemical and sensory changes that occur during cold chain distribution storage and thawing that would improve quality of frozen products.

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